

Investigations of New Techniques for Control of
Smelter Arsenic Bearing Wastes. Volume II
Literature Review

Montana Coll. of Mineral Science and Technology
Butte

Prepared for

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16. ABSTRACT In 1976, the Industrial Environmental Research Laboratory at Cincinnati sponsored a research program at the Mineral Research Center, Montana Tech Alumni Foundation, to investigate a variety of approaches to the fixation of arsenic bearing wastes, particularly smelter flue dusts, to render them harmless to the environment. The enclosed document reports the findings of this work. A comprehensive program was undertaken to investigate various methods of fixing arsenic bearing flue dust wastes produced in smelting of nonferrous metal concentrates. The program was comprised of three principal elements: (1) separation of the arsenic from metal values by leaching; (2) incorporation of the arsenic into a fixation matrix; and (3) leach testing of samples of the fixed product to determine suitability for environmental protection. Stabilization of the arsenic by incorporation in slag matrices and in cements, mortars, clays, and concrete was investigated. The most promising technique found was stabilization by dissolution in the slag matrix to form a solid solution upon cooling.		
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INVESTIGATION OF NEW TECHNIQUES
FOR CONTROL OF
SMELTER ARSENIC BEARING WASTES
VOLUME II
LITERATURE REVIEW

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

The primary nonferrous metals industry is the sole source of arsenic production and the principal source of arsenic released to the environment. In 1976, the Industrial Environmental Research Laboratory at Cincinnati sponsored a research program at the Mineral Research Center, Montana Tech Alumni Foundation, to investigate a variety of approaches to the fixation of arsenic bearing wastes, particularly smelter flue dusts, to render them harmless to the environment.

A comprehensive program was undertaken to investigate various methods of fixing arsenic bearing flue dust wastes produced in smelting of nonferrous metal concentrates. The program was comprised of three principal elements: (1) separation of the arsenic from metal values by leaching; (2) incorporation of the arsenic into a fixation matrix; and (3) leach testing of samples of the fixed product to determine suitability for environmental protection.

Stabilization of the arsenic by incorporation in slag matrices and in cements, mortars, clays, and concrete was investigated. The most promising technique found was stabilization by dissolution in the slag matrix to form a solid solution upon cooling.

David G. Stephan
Director
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ABSTRACT

The Mineral Research Center has completed a comprehensive search of the literature bearing on the fixation of arsenic as the initial activity in the investigation of new techniques for control of arsenic bearing fine dust wastes generated in the smelting of nonferrous metals.

This literature survey on arsenic was undertaken in order to gather information about arsenic that could possibly lead to a technique or techniques for the safe disposal of the arsenic-bearing flue dust generated in the course of smelting nonferrous metal ores that contain arsenic. In precise terms, information was sought on the general chemistry and geochemistry of arsenic, the extractive metallurgy of arsenic and its removal as an impurity from other metallurgical systems, waste water purification, and any existing or researched techniques.

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CONTENTS

Foreword	iii
Abstract	iv
Figures	vi
Tables	vii
Acknowledgements	vii
1. Introduction	1
2. Conclusions	3
3. General Chemistry	9
Chemistry of Elemental Arsenic.	9
Arsenic Trioxide Chemistry	12
4. Geochemistry	28
Geologic Occurrence	28
Environmental Properties and Processes	34
5. Processing Technology	45
Pyrometallurgical Processes	45
Hydrometallurgical Processes	51
Other Processes	56
6. References	64

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FIGURES

<u>Number</u>	<u>Page</u>
1. Arsenic supply-demand curve, 1974	4
2. Arsenic supply-demand curve, 1975	5
3. Flow sheet of As_2O_3 manufacture	7
4. Properties of arsenic trioxides	13
5. Reactions of arsenic trioxide	15
6. Eh-pH diagram of arsenic	25
7. Local geochemical cycle for arsenic	43
8. Flowsheet of iron arsenate precipitation step	53

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TABLES

<u>Number</u>	<u>Page</u>
1. Characteristic Properties of Arsenic	10
2. Characteristic Properties of Al, Si, P, S	11
3. Oxidation Potentials	16
4. Thermodynamic Properties of Arsenic at 298°K	17
5. Thermodynamic Data for Arsenic Compounds and Ions.	18
6. Heat Capacity for As_2O_3	20
7. Aqueous Solubility Products of Metal Arsenates	20
8. Formula for Aqueous Solubility of As_2O_3	21
9. Solubility of As_2O_3	22
10. Solubility of As_2O_5	23
11. Survey of Organic Arsenic Compounds	27
12. Concentration of Arsenic in Rock-Forming Minerals	29
13. Arsenic Minerals	30
14. Arsenic in Igneous Rocks	32
15. Arsenic in Sedimentary Rocks	33
16. Arsenic Content in U.S. Soils	33
17. Coordination Number and Electronegativity of Arsenic and other Elements	35
18. Forms of Arsenic Contamination	40
19. Compilation of Arsenic Leach Data	44
20. Arsenic Glasses	61

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SECTION 1

INTRODUCTION

STATEMENT OF PROBLEM

The Mineral Research Center has completed a comprehensive search of the literature bearing on the fixation of arsenic as the initial activity in the investigation of new techniques for control of arsenic bearing fine dust wastes generated in the smelting of nonferrous metals.

This literature survey on arsenic was undertaken in order to gather information about arsenic that could possibly lead to a technique or techniques for the safe disposal of the arsenic-bearing flue dust generated in the course of smelting nonferrous metal ores that contain arsenic. In precise terms, information was sought on the general chemistry and geochemistry of arsenic, the extractive metallurgy of arsenic and its removal as an impurity from other metallurgical systems, waste water purification, and any existing or researched techniques.

The search included coverage of Chemical Abstracts, Science Citation Index, Engineering Index, and Metallurgical Abstracts. Using this abstracted material, original articles were retrieved, when available, from the libraries of Montana University System; the library of the University of Washington in Seattle, Washington; and the library of Congress in Washington D.C. All literature collected was reviewed. However, only those articles that seemed pertinent to our goal are discussed in this report. For complete coverage of a topic area, the reader should review both the summary discussion and the titles of uncited articles in the bibliography. All the abstracted material has been assembled in one form and is separately available. Since not all articles, patents, etc. could be collected, some of the discussion is based on the abstracts.

A review of the collected literature is presented under various categories in the following sections. Each section summarizes the pertinent literature covering a particular topic or a sequence of topics if related to the major category heading. Each literature article referenced in the discussion section is also listed under the same major heading in the bibliography. Other related articles are also listed in the bibliography even though they are not discussed in the text. Author entries in the bibliography are in alphabetical order under each subject heading or sub-heading. Numbering of references is sequential regardless of subject headings and sub-headings.

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CONCLUSIONS

Arsenic is an unavoidable by-product of the smelting operations when the ore being smelted contains arsenic. Arsenic sublimates very easily, forming arsenic trioxide. This compound is volatile at low temperature (218°C) and is easily captured in the flue dust by the bag house and electrostatic precipitators. The flue dust may contain arsenic as high as 30 percent. A small amount of arsenic is emitted to the atmosphere.

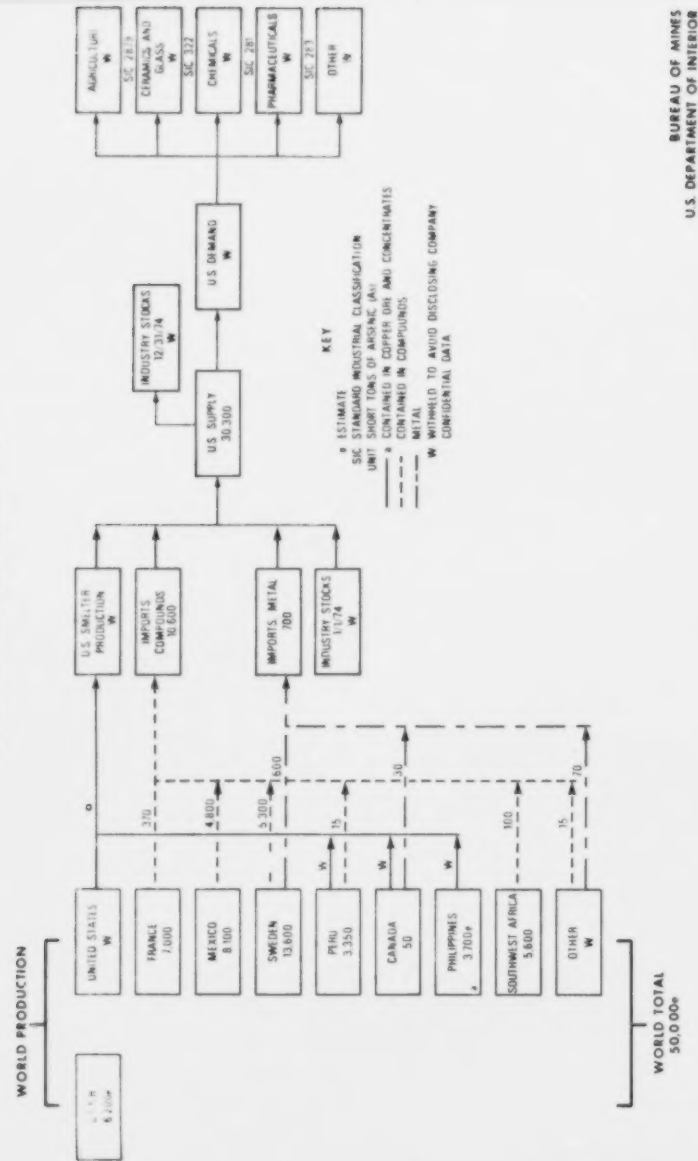
Since the flue dust contains a large amount of arsenic, a highly toxic element, the disposal of the flue dust creates problems associated with the environment. Moreover, a substantial amount of the flue dust remains unprocessed every year, i.e., it is simply stockpiled. The quantity of dust stockpiled has not been disclosed since 1973. In 1973 the estimate was about 12,000 tons, Minerals in the U.S. Economy, 1974 (45a) and 1975 (45b). See Figures 1 and 2.

The stockpiled flue dust should be completely contained because of the danger of arsenic leaching by rain and of flue dust being blown away by wind. This is done to protect the environment from the toxicity generated by arsenic release in the environment. But the storage of arsenic flue dust is a temporary solution to the problem. New ways must be found to detoxify the flue dust so that its disposal is possible.

Since World War II, no orebodies have been worked to solely produce arsenic trioxide. Arsenic is always derived as a by-product of the smelting operations of nonferrous metals. Arsenic trioxide, being highly volatile, ends up in the flue dusts of such plants. The extractive metallurgy of this metal therefore is chiefly concerned with the recovery and treatment of the arsenic-bearing flue dusts. At various smelters, the practice of recovering arsenic after separation from other constituents in the flue dust is being abandoned in preference to storing it or shipping it for further processing to a different plant. There is only one plant in the United States, American Smelting and Refining Company plant at Tacoma, Washington, that treats the flue dust for the recovery of the arsenic and its compounds.

Although arsenic-bearing flue dust carries large concentrations of other base metals like lead, zinc, cadmium, and copper, the economics of arsenic recovery are such that it is unprofitable to even ship it a short distance for reprocessing. That was the problem encountered by the Boliden smelter in Sweden. Hence arsenic is an unwanted by-product of the nonferrous metallurgical industry in the U.S. and abroad. For industrial operations, arsenic

ARSENIC SUPPLY-DEMAND RELATIONSHIPS-1974



(Reprinted from Minerals in the U.S. Economy, Bureau of Mines, 1974). (45a).

Figure 1. Arsenic Supply-Demand Relationship - 1974

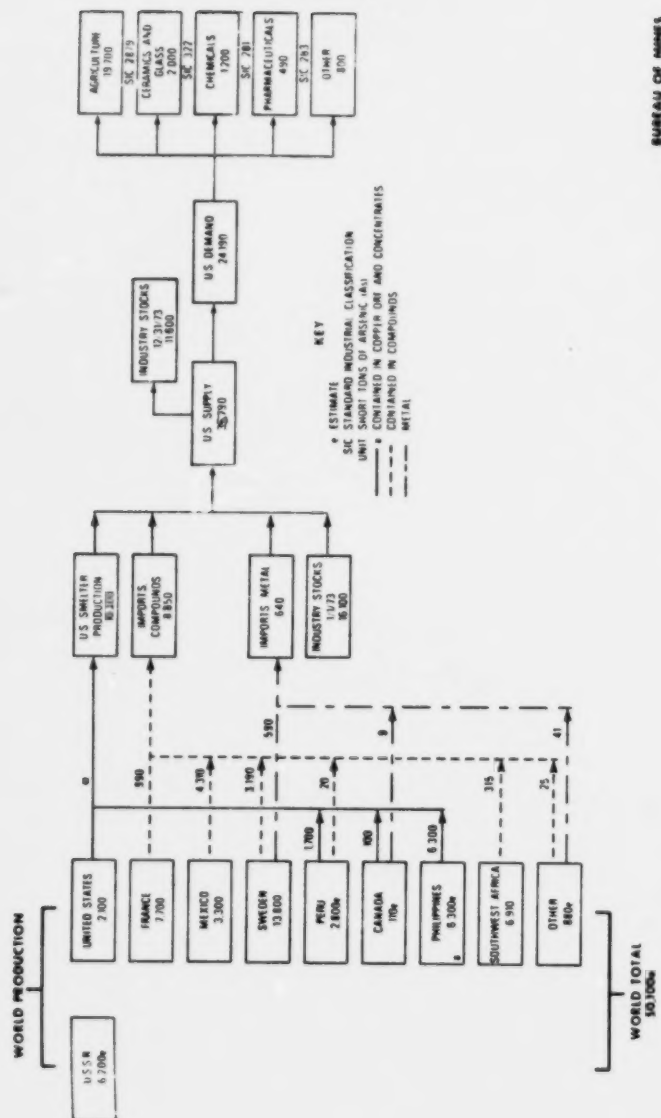
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(Reprinted from Minerals in the U.S. Economy, Bureau of Mines, 1975). (45b)

Figure 2. Arsenic Supply-demand Relationship - 1975

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is a waste problem that requires a safe disposal technique. This is not to say that the arsenic flue dusts are never worked to extract all the metal values including arsenic. In fact, the Anaconda smelter has shipped its arsenic flue dust to the ASARCO smelter in Tacoma, Washington for further processing. But over the years, the nonferrous industry has accumulated a large amount of the arsenic flue dust.

The various methods employed for extracting white arsenic in commercial plants are fairly well known and have been carefully reviewed from time to time, Smith, 1926 (58), Encyclopedia of Chemical Technology, 1947 (36), 1963 (37), and Hayward, 1957 (28). White arsenic (Figure 3) has been made from smelting flue dusts of copper and lead smelters as well as roasting arsenical gold ores.

Recent figures are not available on the market structure of arsenic in the U.S. in terms of production. In 1968, 28,000 tons of arsenic (As) were consumed in the U.S. Of this amount, 8000 tons were derived from treating the flue dust, speiss, and sludge of the nonferrous industry. In 1968, two thirds of the domestic demand was met by the imports, chiefly from Sweden, Mexico, and France, Davis, 1971 (700).

Arsenic in its +3 valence state, arsenates, arsenites, arsine, and arsenic trioxide are all toxic substances, arsine being by far the most toxic of the arsenic compounds, Valle et al., 1960 (63). The fatal dose of arsenic trioxide is between 70 and 180 mg although the toxic symptoms and reactions can occur at much lower doses. It is interesting to note here the talk of the people who worked in arsenic "kitchens" (arsenic condensing chambers) of the old days of eating a pinch of the "stuff" to build up an immunity against arsenic.

The highly toxic nature of arsenic compounds calls for special precautions in order to preserve health among the workers in plants producing or processing any of the arsenic compounds. In a survey conducted in the Converter Departments of certain smelters in the western U.S., a potential health hazard was noted, Wagner, et al., 1975 (716). "If the high airborne arsenic concentration observed in the survey were truly indicative of the employee exposure, these conditions could result in a potential for arsenic-induced cancer." However, it was noted that the potential for such cancers is extremely difficult to assess because of the uncertainty in the dose-response relationship of arsenic-induced cancer. The presence of sulfur dioxide or other unidentified chemical, varying concomitantly with arsenic exposure, could throw these observations off-balance, Lee and Fraumeni, Jr., 1969 (41).

Arsenical dusts may produce dermatitis, bronchitis, and irritation to the upper respiratory tract. Medical injection of arsenic has produced keratoses and cancer of the skin, Sullivan, 1969 (714). Localized areas around the operations of mining, milling, and smelting of the arsenical ores may be the recipients of arsenic emissions from these operations. Therefore, arsenical poisoning is not limited to persons in daily contact with it in their work, but extends in some degree to the public in general. The public

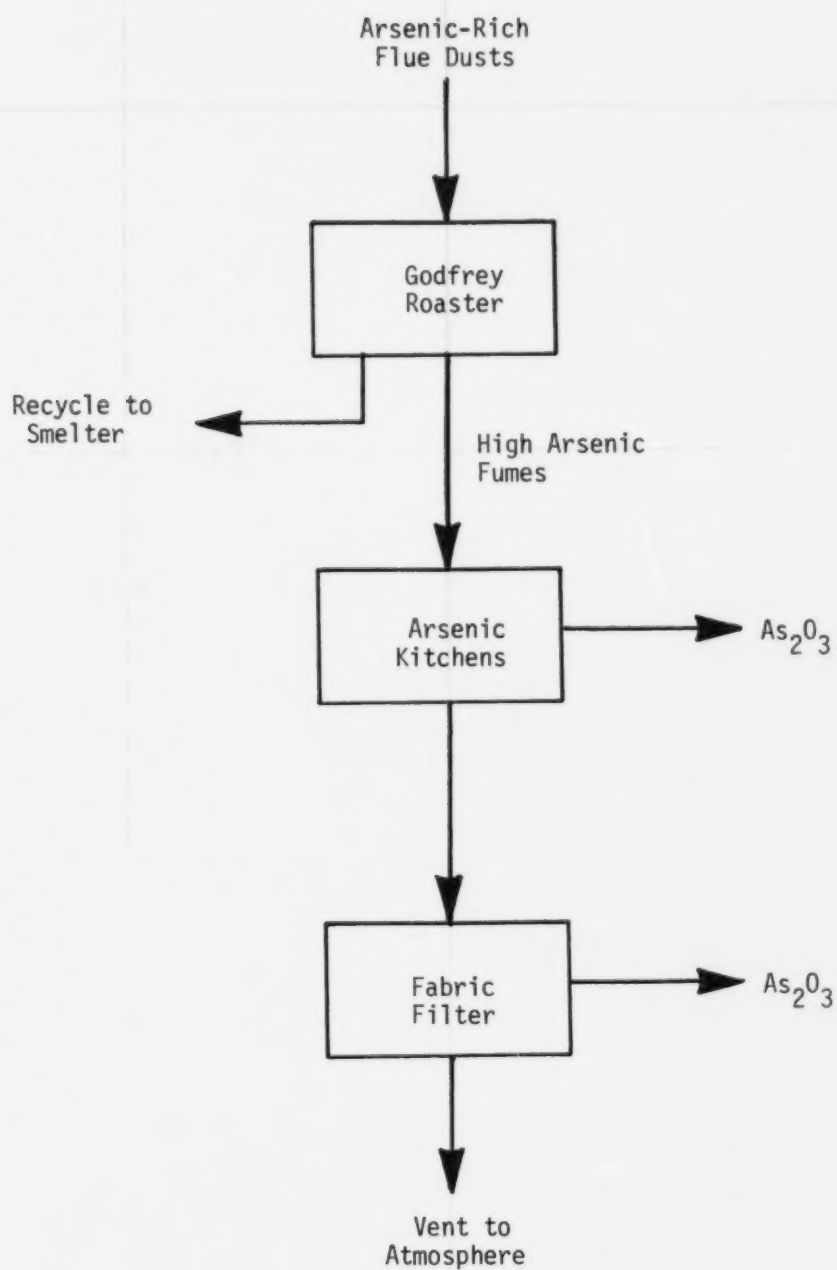


Figure 3. Flowsheet of As_2O_3 Manufacture.

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health standard for arsenic (As) in drinking water is 0.05 mg/liter while the provisional limit for As₂O₃ in air is 0.005 mg/cubic meter as As.

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Arsenic trioxide, or "white arsenic" as it is commonly known, can be particularly insidious. White arsenic is odorless and tasteless. Indeed in previous centuries, it has been the poison of choice. It was difficult to recognize poisoning by "white arsenic" because the symptoms of that poisoning were very common and could be interpreted as some other sickness or disease. With the advent of the twentieth century and remarkable progress in chemical analysis, incidence of intentional "white arsenic" poisoning has decreased rapidly, Harrison et al., 1958 (27).

The problem we address here is not so much of direct exposure of arsenic toxicity to humans but one of introducing arsenic and its compounds into the ecocycle and the subsequent effects on the environment. There are many notable episodes of arsenic pollution related to mining and smelting activities here in the U.S. and abroad, NAS Report, 1976 (709).

The solution to this problem is to treat arsenic flue dust so that it is rendered non-toxic and can be disposed of in a safe manner without any danger to humans, plants, animals, and the other ecosystems.

As environmental quality regulations are implemented, quantities of industrial wastes increase rapidly with arsenic being no exception, especially in light of its toxic and hazardous nature, Lindsey, et al., 1976 (707). Their criteria for the safe disposal of the waste material is to treat the waste physically, chemically, or biologically to permit recycling or recovery, and to treat the waste so as to detoxify it.

Possible treatments in terms of the control technology for hazardous wastes disposal are suggested by Schomaker, 1976 (713), i.e., minimize the impact of placing such wastes in the ecocycle and let the natural processes of stabilization take over, or totally prevent such wastes from entering the ecocycles. Examples are:

- | | |
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| 1) natural soil processes, | 4) encapsulation, |
| 2) physical, chemical, and biological treatments, | 5) stabilization, and |
| 3) isolation in underground cavities, | 6) chemical fixation. |

Fixation possibilities are described in the report under various topical headings. It must be realized that fixation of arsenic in an environmentally safe form has not been demonstrated by any of the past literature. Present industrial practice consists of containment by storage of the arsenical flue dust.

While the emphasis is on fixation of arsenic in flue dust, the economic importance of recovering metal values in the flue dust cannot be dismissed. Therefore the experimental phase addressed a plan of hydrometallurgical separation of arsenic from the other constituents in flue dust.

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SECTION 3

GENERAL CHEMISTRY

Since the chemistry of arsenic is very complex, initial attention was focused on the general chemistry of elemental arsenic, including electronic structure, bonding, common oxidation states, electronegativity, atomic radii, occurrence in nature and common arsenic forming compounds. It is important not only to describe the chemistry of arsenic compounds in general but to describe in detail the chemistry of arsenic trioxide, a potentially hazardous pollutant to the environment. Characteristic properties in the solid, gaseous and aqueous phases will be examined. Properties of selected organic compounds of arsenic are briefly addressed.

CHEMISTRY OF ELEMENTAL ARSENIC

Arsenic is classified chemically as a metalloid. It possesses five electrons ($4s^2 4p^3$) in its outside main energy level, Keenan and Wood, 1973 (110). Arsenic is dominantly a trivalent element and tends to form three electron-pair bonds approximately at right angles. This leaves an ns^2 lone pair. However, some hybridization occurs and results in distortion towards more nearly tetrahedral bonds. All five valence electrons may participate in bonding, d-hybridization resulting in bipyramidal, square pyramidal, and octahedral sets of bonds, Heslop and Robinson, 1969 (103).

In many arsenic compounds the metal is characterized as formally having a charge number of plus five or plus three. The plus three state is stable with respect to disproportionation to the plus five state and the zero state, Heslop and Robinson, 1969 (103). The bonding is often mainly covalent and its tendency towards nonmetallic character is demonstrated in compounds with true metals. In a compound such as Na_3As the Group VB metal evidently accepts electrons to achieve a formal charge of minus three.

If we compare characteristic properties of arsenic, presented in Table 1, to the elements Al, Si, P, and S, presented in Table 2, it becomes apparent that most of the elements exhibit several oxidation states. This comparison is of interest since arsenic appears to be related with these elements in various laboratory and natural systems. For oxidation states of +4 and over, cations will exist in aqueous solution as covalently bonded complex ions. The electronegativities given in Table 2 illustrate that sulfur has a relatively high electron affinity which is characteristic of a nonmetal. The electron affinity decreases down to aluminum, which does have properties similar to a metal. From these data it is apparent that the electronegativity of arsenic is within the limits set by sulfur and aluminum. Since phosphorus

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TABLE 1. CHARACTERISTIC PROPERTIES OF ARSENIC

Arsenic		Common Forms
Common Oxidation State	+3, +5, -3	Lead arsenite $Pb(AsO_2)_2$ Loellingite Fe_2+xAs_4-x
Electronegativity*	2.0	arsenic pentoxide As_2O_5 arsenic trichloride $AsCl_3$ arsenic trioxide As_2O_3 arsenopyrite or mispickel $FeAs_2 \cdot FeS_2$ orpiment As_2S_3 ortho-arsenic acid $H_3AsO_4 \cdot \frac{1}{2}H_2O$
Ionic Radius, Å	0.46 (+5) 0.58 (+3) 2.22 (-3)	calcium arsenate $Ca_3(AsO_4)_2$ Paris green $3Cu(AsO_2)_2 \cdot Cu(C_2H_3O_2)_2$ cupric arsenite $CuHAsO_3$ realgar As_2S_2
Occurrence	Elemental and combined form in nature	α - dimorphite As_4S_3 sodium arsenite $NaAsO_2$ lead arsenate $Pb_3(AsO_4)_2$ arsine AsH_3

*Pauling's

Table 1 was composed from the following reference material: Weast, 1970 (151). Dull, Metcalf, and Williams, 1962 (89); Sargent-Welch Scientific Company, 1968 (712); criteria for a recommended standard: Occupational Exposure to Inorganic Arsenic, 1973 (715); and Smith, 1973 (141).

TABLE 2. CHARACTERISTIC PROPERTIES OF Al, Si, P, AND S.

	Aluminum	Silicon	Phosphorus	Sulfur
Common Oxidation States	+3	+2, +4, -4	+3, +4, +5, -3	+2, +4, +6, -2
Electronegativity*	1.5	1.8	2.1	2.5
Ionic Radius, Å	0.51 (+3)	0.42 (+4) 0.65 (+1) 2.71 (-4) 3.84 (-1)	0.35 (+5) 0.44 (+3) 2.12 (-3)	0.30 (+6) 0.37 (+4) 1.84 (-2) 2.19 (+2)
Occurrence	Does not exist free in nature.	Does not exist free in nature.	Does not exist free in nature.	Elemental and combined form in nature.

*Pauling's

The data of Table 2 were compiled from the following references: Weast, 1970 (151); Dull, Metcalfe, and Williams, 1962 (89); and Sargent-Welch Scientific Company, 1968 (712).

and arsenic belong to the same family, the increase in atomic number is accompanied by only a slight decrease in the electronegativity. Therefore, it is not surprising to observe that arsenic exhibits metallic and non-metallic properties that are quite similar to those of phosphorus.

It should also be pointed out that the comparison of ionic radii of arsenic and phosphorus from Tables 1 and 2 indicates that as the atomic number increases within the family there is an increase in the ionic size. In addition, it is also evident that within the Group VA elements, greater positive charge produces markedly smaller cations while greater negative charge produces only slightly larger anions. These similarities and differences in size and charge will significantly influence the possible substitution of arsenic for these elements in various crystal structures.

ARSENIC TRIOXIDE CHEMISTRY

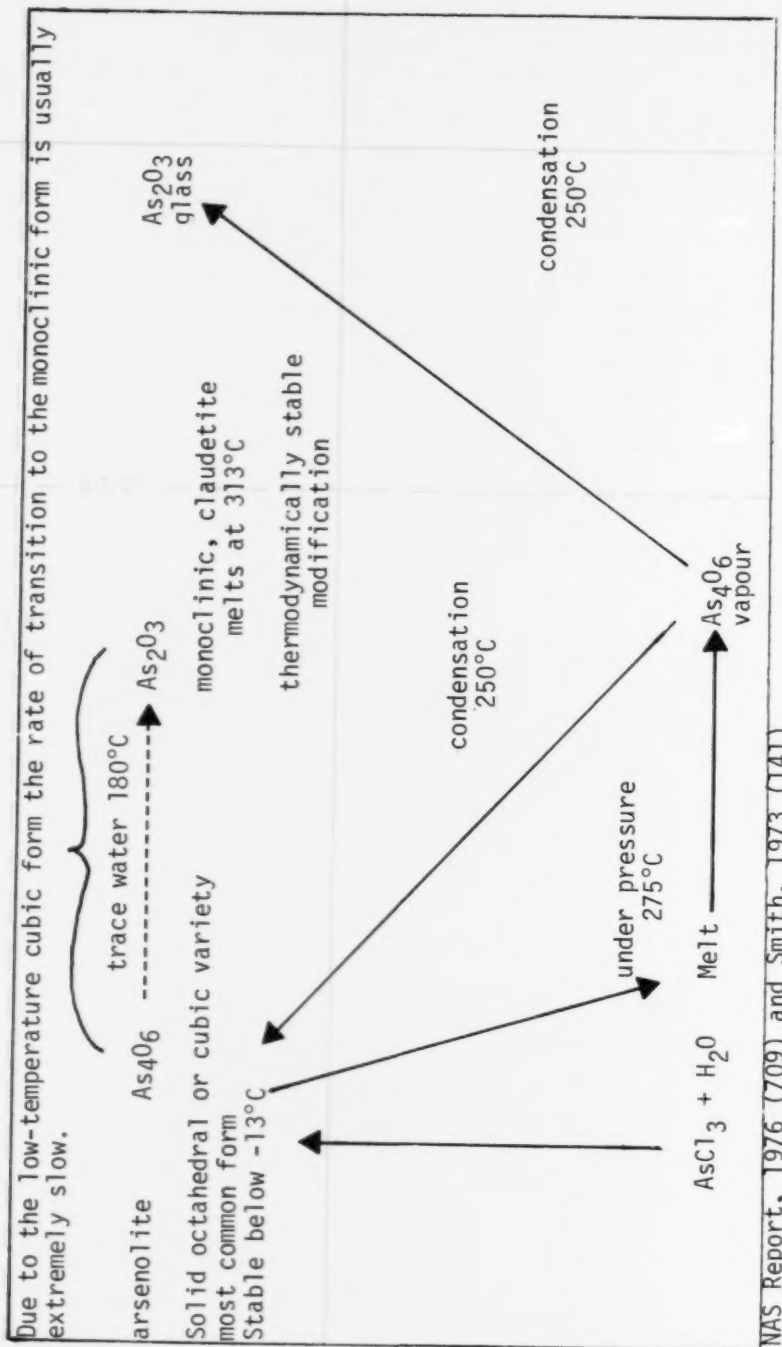
A discussion of arsenic trioxide summarized from the NAS Report, 1976 (709) is presented. Arsenic is produced in the United States as a by-product of the smelting of nonferrous metal ores. Arsenic trioxide (As_2O_3) is formed when metallic arsenides or arsenic-containing sulfides are roasted in air. The vapors condense in the flues and on the walls of the stacks as a powder. Arsenic is found in appreciable quantities in copper ores and, thus, during the smelting process considerable amounts of arsenic find their way into the flue dust.

Properties in Solid and Gaseous Phases

The properties and structures of As (III) are presented in Figure 4. There are two monoclinic forms of arsenious oxide (claudetite I and II) in which alternate arsenic and oxygen atoms are linked into sheets making open macromolecular structures. The amorphous, glassy form of arsenious oxide is uniform, however the macromolecular structure is irregular. In all the structures, pyramidal AsO_3 groups share oxygen atoms, but the connecting of the pyramids is different in the various modifications. The cubic and monoclinic forms have very similar stabilities in regard to the elements. Formation of cubic arsenolite by crystallization from aqueous solutions appears to be controlled by kinetic factors. Interconversion of various forms of As (III) is slow, due to rearrangements and the breaking of many As-O bonds. Changes are catalyzed by water and it is assumed As-O bonds are protonated and the AsOH units can reform into a new pattern more easily than the original AsOAs units, Smith, 1973 (141).

Properties in Aqueous Phases

The aqueous chemistry of As (III) discussed below has been abstracted from Smith, 1973 (141). As (III) is not very soluble in water (0.104 mol As_2O_3 per kg water at $25^\circ C$). Increasing the HCl concentration decreases the solubility reaching a minimum (0.075 mol per kg water) at approximately 3M HCl. Increasing the HCl concentration further results in the solubility. Species with As-Cl bonds are presumed to be formed at high HCl concentrations.



NAS Report, 1976 (709) and Smith, 1973 (141).

Figure 4. Properties of As_2O_3

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The predominant species in neutral or acid solution is probably $\text{As}(\text{OH})_3$. The oxide As_2O_3 is obtained upon crystallization from these aqueous solutions. In basic solutions $\text{As}(\text{III})$ is much more soluble, apparently forming species of this nature $(\text{AsO}(\text{OH})_2)^-$, $(\text{AsO}_2(\text{OH}))_2^{2-}$ and AsO_3^{3-} , but not the specie AsO_2^- . There does not seem to be any substantial evidence for the formation of polymerized species, such as $\text{As}_2\text{O}_5^{4-}$, $\text{As}_3\text{O}_6^{3-}$.

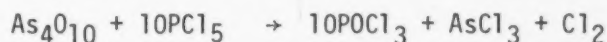
Salts known as arsenites are obtained when alkaline solutions of $\text{As}(\text{III})$ oxide are evaporated. The chemistry of arsenites is scanty but structures appear to consist of metal ions and pyramidal AsO_3 groups joined into sheets or chains like those of the macromolecular forms of $\text{As}(\text{III})$ oxide. Yellow silver arsenite (incontrast to arsenate which is brown in appearance) and copper arsenite may be precipitated from neutral solutions, Smith, 1973 (141).

$\text{As}(\text{III})$ oxide is a starting basis for the preparation of many other arsenic compounds. The reactions of $\text{As}(\text{III})$ oxide are illustrated in Figure 5.

The trioxide As_4O_6 or As_2O_3 is amphoteric, capable of acting either as an acid or base. This is clearly demonstrated when the oxide reacts with alkali and carbonates to form arsenites (AsO_3^{3-}), and also reacts with concentrated sulfuric acid to form $(\text{AsO})_2\text{SO}_4$, arsonium sulfate. At 100°C arsenic (III) reacts with sulfur trioxide to form $\text{As}(\text{III})$ sulfate. $\text{As}(\text{III})$ can be oxidized to $\text{As}(\text{V})$ by ozone, hydrogen peroxide, halogens, or nitric acid. In addition, $\text{As}(\text{V})$, As_4O_{10} or As_2O_5 , a white deliquescent solid, can be made by heating the hydrated arsenic acid.



The oxide will decompose to $\text{As}(\text{III})$ upon heating to red heat. This solid oxide of arsenic is the anhydride of orthoarsenic acid and can act as an oxidizing agent, e.g.,



Arsenous acid, H_3AsO_3 or $(\text{HO})_3\text{As}$, a weak acid ($K_1 = 6 \times 10^{-10}$) is only known in solution. In a hot sodium hydroxide solution this acid will dissolve and upon evaporation sodium arsenite Na_3AsO_3 will form. Other pertinent facts, pointing out the existence of this acid is that the acid reacts with alcohols to produce esters, $\text{As}(\text{OR})_3$ where R can be substituted for a methyl, ethyl or propyl group.

Orthoarsenic acid, H_3AsO_4 or $(\text{HO})_3\text{AsO}$, is a white solid material. At 36°C it exhibits its melting point. It is quite soluble in water. The acid constants are as follows,

$$K_1 = 5.6 \times 10^{-3}$$

$$K_2 = 1.7 \times 10^{-7}$$

$$K_3 = 3.0 \times 10^{-12}$$

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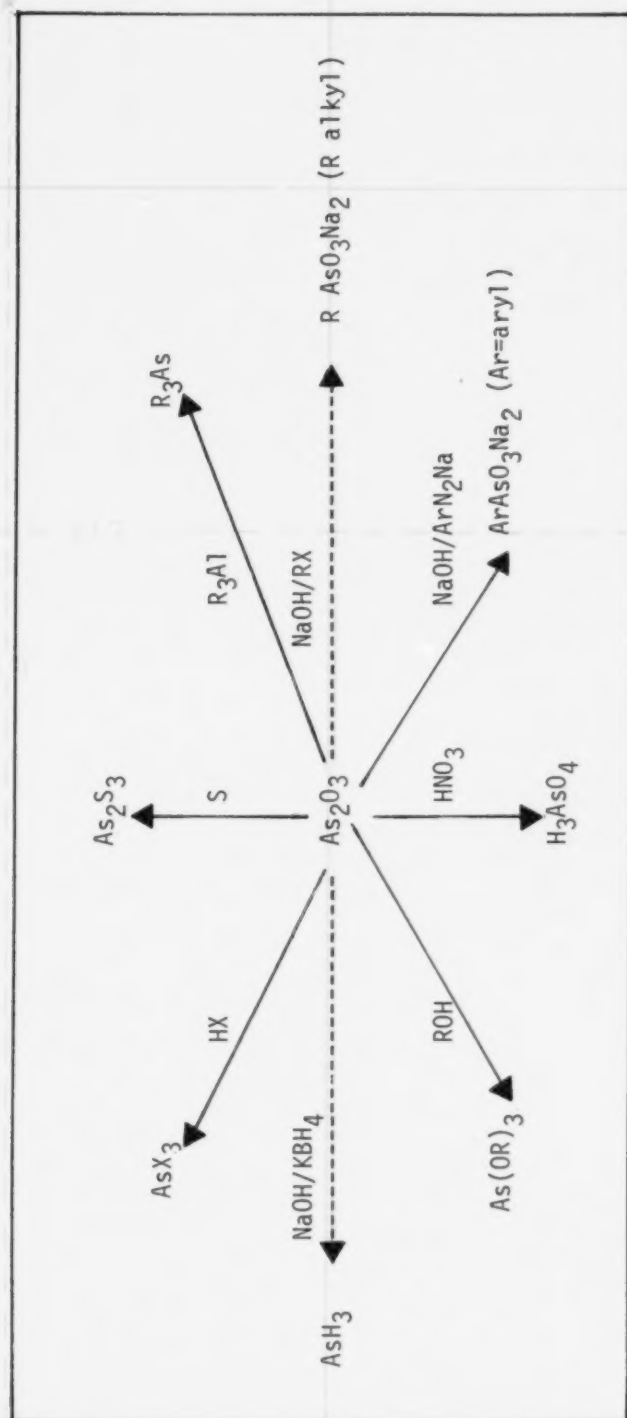
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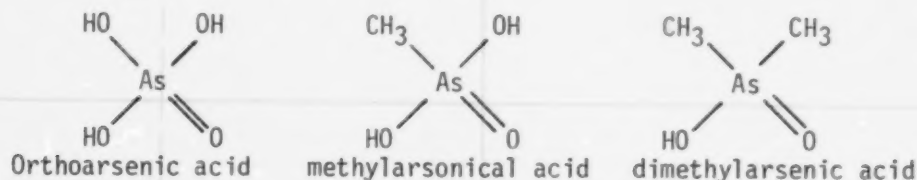
Smith, 1973 (141)

Figure 5. Reactions of Arsenic Trioxide

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The formulation of condensed acids of orthoarsenic acid is also possible. Some methyl derivatives of orthoarsenic acid exist in the forms illustrated below, Demitras et al., 1972 (87).



According to Smith, 1973 (141), most binary compounds of arsenic either react with water or are insoluble in it. The chemistry of aqueous solutions of arsenic is the chemistry of oxyions, or complexes with ligands other than water: species $\text{E}(\text{H}_2\text{O})_n^{\text{m}+}$ are seldom formed. In an aqueous environment many arsenites and arsenates are produced. Arsenic usually occurs in anionic species. Some common oxidation-reduction reactions of arsenic are presented in Table 3. As (V) is a weak oxidizing agent, however it reacts stronger in acid than in alkaline solutions. Neither of the oxidation states III or V for arsenic disproportionates in solution.

TABLE 3. OXIDATION POTENTIALS

Oxidation-Reduction Data [$E^\circ = 0$ for H^+ ($a=1$)/ H_2]	Volts
1. $\text{As}(\text{s}) + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{AsH}_3(\text{g})$	-0.239
2. $\text{HAsO}_2 + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{As}(\text{s}) + 2\text{H}_2\text{O}$	+0.247
3. $\frac{1}{2}\text{As}_2\text{O}_3(\text{s}) + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{As}(\text{s}) + \frac{3}{2}\text{H}_2\text{O}$	+0.234
4. $\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HAsO}_2 + 2\text{H}_2\text{O}$	+0.559
5. $\text{AsO}_2^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightleftharpoons \text{As}(\text{s}) + 4\text{OH}^-$	-0.68
6. $\text{AsO}_4^{3-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{AsO}_2^- + 4\text{OH}^-$	-0.67

Additional properties of arsenic in an aqueous phase can be ascertained from the thermodynamic data or arsenic and selected arsenic compounds. These data are presented in Tables 4 through 10.

A discussion of As (V) and arsenates has been abstracted from Smith, 1973 (141). The following equations demonstrate the reaction of As (III) oxide and concentrated nitric acid.

TABLE 4. THERMODYNAMIC PROPERTIES OF ARSENIC AT 298°K.

	ΔH_f° (KJ mol ⁻¹)	ΔG_f° (KJ mol ⁻¹)	$H^\circ_{298} - H^\circ$ (KJ mol ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	C_p (J mol ⁻¹ K ⁻¹)	Vapor pressure at b.p. (atm)
As(s)	0	0	5.129	35.1	24.6	
As(g)	302.5	261.1	6.196	174.1	20.8	
As ₂ (g)	222.2	172.0	9.418	239.3	35.0	5.5x10 ⁻⁴
As ₄ (g)	143.9	92.5		313.8		1.0

TABLE 5. THERMODYNAMIC DATA OF ARSENIC COMPOUNDS AND IONS

Formula	Description	State	ΔH_f° , 298°K (k cal/mole)	ΔG_f° , 298°K (k cal/mole)	$\log K_f$	ΔS° , 298°K (e.u.)	C_p (298°K)
AsO ⁺	std. state, hyp.	aq.	-39.1	28.69			
AsO ₂ ⁻	"	aq.	-83.7	61.33			
AsO ₄ ⁻³	"	aq.	-208	-152	111.4	34.6	
As ₂ O ₅		c	-218.6	-184.6	135.41	25.2	27.85
As ₂ O ₅ ·4H ₂ O		aq.	-224.6				
3As ₂ O ₅ ·5H ₂ O		c	-500.3				
As ₄ O ₆	octahedral	c	-1007.5				
	monoclinic	c, II	-313.94	-275.36	201.835	51.2	45.72
		c, I	-312.8				
As ₂ O ₃ ·As ₂ O ₅		aq.	-299.4				
HAso ₂	std. state, hyp.	c	-351.1				
		aq.	-109.0	-96.25	70.550	30.3	

TABLE 5. THERMODYNAMIC DATA OF ARSENIC COMPOUNDS AND IONS (Continued)

Formula	Description	State	ΔH_f° , 298°K (k cal/mole)	ΔG_f° , 298°K (k cal/mole)	$\log K_f$	ΔS° , 298°K (e.u.)	C_p (298°K)
HAsO_3^{2-}	m=1	aq.	-157.1				
HAsO_4^{2-}		aq.	-214.8	-169	123.9	0.9	
H_2AsO_3^-		aq.	-170.3				
H_2AsO_4^-	std. state, hyp. m=1	aq.	-216.2	-178.9	131.13	28	
H_3AsO_3	std. state, hyp. m=1	aq.	-177.3	-152.9	112.07	47.0	
H_3AsO_4	" " " " " " " "	c	-215.2				
	" " " " " " " "	aq.	-214.8	-183.8	134.72	49.3	

Rossini, et al., 1952 (132)

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TABLE 6. HEAT CAPACITY DATA FOR As_2O_3

T (°C)	Cp (joule/g)
-150	0.230
-100	0.318
0	0.489
40	0.509

NRC, 1929 (121).

TABLE 7. AQUEOUS SOLUBILITY OF METAL ARSENATES

Compound	Solubility Product constant, K_{sp}	AsO_4^{3-} concentration (moles/liter)
$\text{Ca}_3(\text{AsO}_4)_2$	6.8×10^{-19}	1.8×10^{-4}
$\text{Mg}_3(\text{AsO}_4)_2$	2.1×10^{-20}	9.1×10^{-5}
$\text{Zn}_3(\text{AsO}_4)_2$	1.3×10^{-28}	2.1×10^{-6}
$\text{Cd}_3(\text{AsO}_4)_2$	2.2×10^{-33}	2.3×10^{-7}
$\text{Pb}_3(\text{AsO}_4)_2$	4.1×10^{-36}	6.6×10^{-8}
AlAsO_4	1.6×10^{-16}	1.2×10^{-8}
FeAsO_4	5.7×10^{-21}	7.6×10^{-11}

Chukhlantsev, 1956 (82), (83).

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TABLE 8. FORMULA FOR AQUEOUS SOLUBILITY OF As_2O_3

	Range	A	B	C
As_2O_3	0 to 100	16,470	-0.473	549.3
	$T^\circ\text{C}$	S		
	0	1.21		
	25	2.05		
	98.5	8.18		

$$\log_{10} \frac{1}{x} = \frac{0.05223}{T} A + B$$

where x = mole fraction of the unhydrated As_2O_3

A = motal heat of solution (joules)

B = numerical constant

C = $\frac{\text{molecular weight of solute} \cdot 100}{\text{molecular weight of water} \cdot n}$

n = number of moles solute formed in solution from 1M of the solid solute ($n = 2$ for As_2O_3)

$$S = \frac{c}{1/x - T}$$

where S = grams solute/100 grams water

NRC, 1928 (121).

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TABLE 9. SOLUBILITY OF As_2O_3

Water

Gms. As_2O_3 per 100 gms. sat. solution
in aq. sol. of:

t°	Mols. Acid per liter	H_3AsO_4	H_3PO_4	H_2SO_4	HCl	HClO_4
25	1.0	1.62	1.62	1.55	1.83	1.71
"	5.0	1.10	0.94	0.54	...	0.43
"	7.5	1.23	0.63	0.25	5.02	0.18
60	1.0	3.50	3.50	3.26	3.64	3.47
"	5.0	2.63	2.09	1.19	...	..0
"	7.5	2.10	1.57	0.78	15.43	0.42
98-99	1.0	8.45	8.46	7.27	...	6.69
"	5.0	5.08	4.51	2.62	...	1.88
"	7.5	4.36	3.02	1.48	25.92	0.84

Acids

Gms. per 100 gms. H_2O		Gms. per 100 gms. H_2O		Gms. per 100 gms. H_2O	
HCl	As_2O_3	HCl	As_2O_3	HCl	As_2O_3
0.0	2.047	3.647	1.812	11.56	1.468
0.1466	1.986	3.775	1.818	12.58	1.525
0.2991	1.988	5.562	1.672	13.68	1.563
0.3756	1.998	7.586	1.622	15.86	1.822
1.109	1.962	9.482	1.614	17.87	1.939
2.564	1.879	10.58	1.592	29.54	9.79

NaOH

Gms. per 100 gms. H_2O		Gms. per 100 gms. H_2O		Gms. per 100 gms. H_2O	
NaOH	As_2O_3	NaOH	As_2O_3	NaOH	As_2O_3
0.0	0.2047	2.013	1.133	12.00	4.15
0.1200	0.2447	3.81	1.289	17.55*	3.84
0.2801	0.3050	5.609	1.592	24.00	8.39
0.4013	0.3466	4.009	1.788	34.82*	7.79
0.8002	0.510	6.006	2.39	69.9*	11.98
1.200	0.663	8.042	3.22	2.05*	33.0

Linke, 1958, 1965 (116)

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TABLE 10. SOLUBILITY OF As_2O_5

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Water

t°	Gms. As_2O_5 per 100 Sat. Sol.	Solid Phase	t°	Gms. As_2O_5 per 100 Sat. Sol.	Solid Phase
-5	10.6	Ice	-10	36.2	$\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$
-10	15.6	"	0	37.3	"
-20	21.3	"	+10	38.3	"
-30	25.1	"	20	39.7	"
-40	27.8	"	29.5	41.4	" + $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$
-50	29.9	"	40	41.6	$3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$
-59(Eutec.)	31.7	Ice + $\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$	60	42.2	"
-50	32.6	$\text{As}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$	80	42.9	"
-40	33.5	"	100	43.3	"
-30	34.4	"	120	43.7	"
-20	35.4	"	140	44.5	"

Linke, 1958, 1965 (116)

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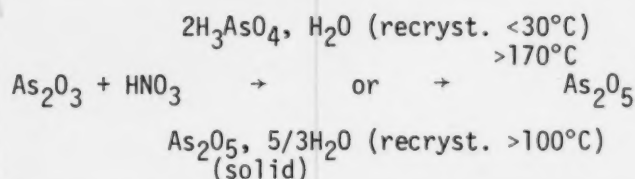
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These reactions are temperature dependent. The reaction produces a solution from which either of two solids can be recrystallized. The hydrate $2\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ is composed of double sheets of AsO_4^{3-} tetrahedra and water molecules joined by hydrogen bonds. $\text{As}_2\text{O}_5 \cdot 5/3\text{H}_2\text{O}$ has a structure in which infinite band-like molecules $(\text{H}_5\text{As}_3\text{O}_{10})\text{X}$ are linked by short hydrogen bonds ($\text{H} \dots \text{O}$ 240-245 pm). Two of the arsenic atoms in the repeating unit have the tetrahedral co-ordination structure (As-O, 169.3 pm) and the other atom is six-co-ordinate (As-O, 182 pm). When heated to constant weight at 350°C both solids yield analytically pure As_2O_5 (ΔH_f° , -924.9; ΔG_f° , -782.4 kJ mol⁻¹; S° , 105.5; Cp, 116.5 J mol⁻¹ K⁻¹). Mixed crystals (As, P) $_2\text{O}_5$ are produced which may contain up to 50 mol % P_2O_5 .

In some arsenates, the AsO_4^{3-} tetrahedra are connected by cations or by systems of hydrogen bonds. The tetrahedra are sometimes distorted, with As-O distance from 165 to 175 pm. It has been suggested that shorter bonds are connected with hydrogen atoms (As-OH). It appears movement within the hydrogen bond system of the dihydrogen arsenates MH_2AsO_4 (M = K, Rb₃, Cs, NH₄) functions as a mechanism for ferroelectric properties.

In other groups, the AsO_4^{3-} tetrahedra are linked by the sharing of corners. Cyclic $\text{As}_3\text{O}_9^{3-}$ ions have been established in the potassium salt $\beta\text{-K}_3\text{As}_3\text{O}_9$. Characteristic of sodium meta-arsenate are chains with repeating trimeric units. The structure of lithium arsenate is diopside-like chains, with a repeating dimeric unit. Sodium meta-arsenate and lithium arsenate exhibit fibre-like properties. It has been suggested that synthetic arsenates are ion-exchange materials.

The structural chemistry of the arsenates in a broad sense is similar to that of phosphates and silicates. It is possible to have some isomorphous replacement of arsenic by phosphorus. However, not all arsenates have the same structures as the corresponding phosphates. Phosphate and silicate frameworks are more common than condensed As-O frameworks and As-O-As bonds are evidently broken in aqueous solution. A case in point is that arsenic acid is tribasic (at 298 K; $\text{pK}_1 = 2.12$; $\text{pK}_2 = 6.19$; $\text{pK}_3 = 11.5$) possessing dissociation constants similar to phosphoric acid. In addition, alkali metals give two series of acid salts and lose water on heating.

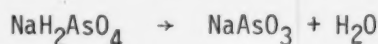


Figure 6 illustrates an Eh-pH graph developed on the basis of thermodynamic data. The Eh-pH diagram for arsenic at 25C and 1 atm, with total arsenic 10^{-5} mole/liter and total sulfur 10^{-3} mole/liter. In the cross-hatched area, the solid forms are enclosed by parentheses and the solubility

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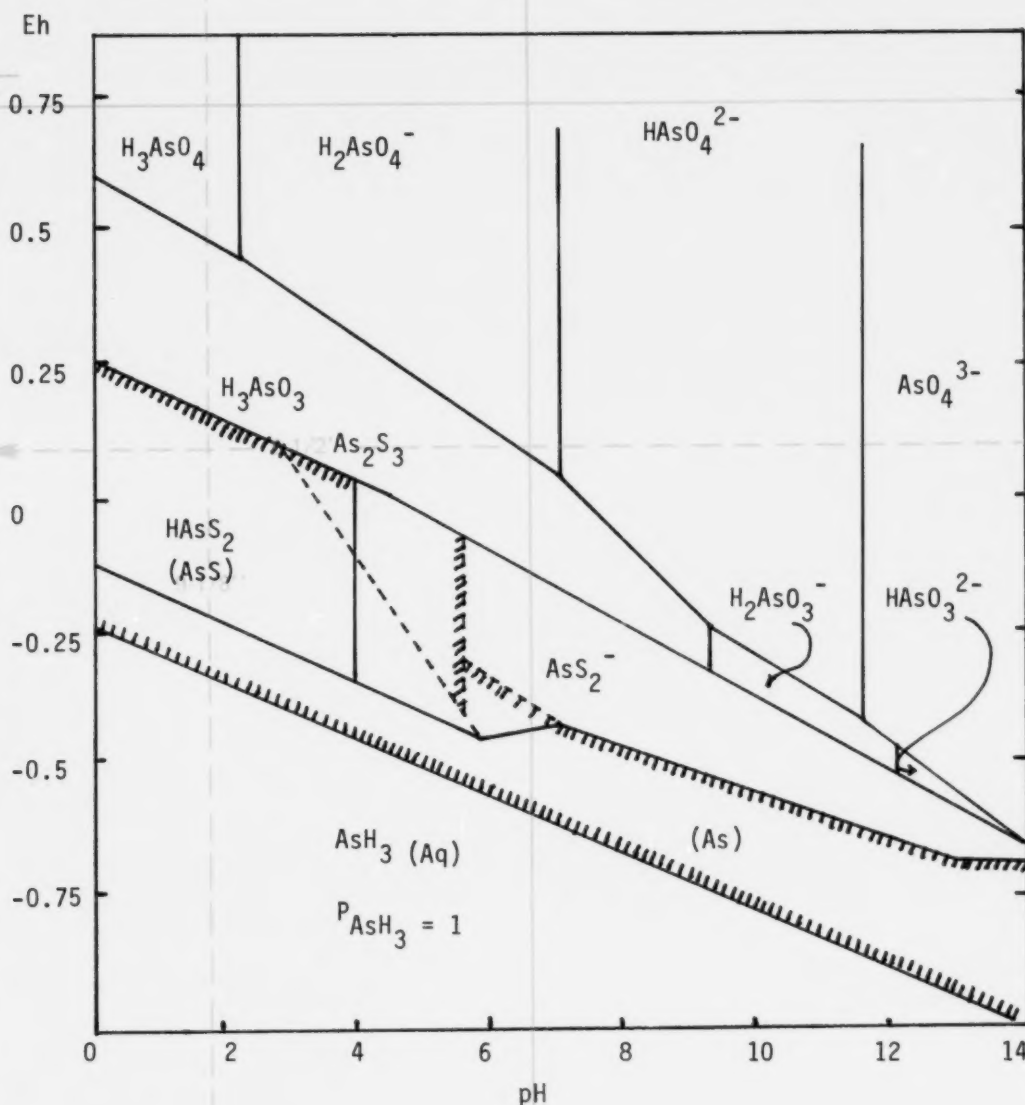
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Reproduced from Arsenic (1977) with the permission of the National Academy of Sciences, Washington, D.C.

(Reprinted from NAS Report, 1976). (709).

Figure 6. Eh-pH diagram of Arsenic

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of these salts is less than 10^{-5} mole/liter. Soluble arsenic species are represented in the other areas. The fixed limits between species indicate Eh-pH values where the substances are at equal concentration.

Since arsine is postulated to be generated in the soils and sediments, its chemistry is of some interest. The action of dilute acid on calcium arsenide gives 14% yield of arsine, AsH_3 or arsenic hydride. Arsine can also be made by an alternative method by the action of zinc and acid on almost any simple, soluble arsenic compound.

Arsine is relatively unstable thermally and decomposes rapidly at 300°C . If arsine is mixed with zinc and acid and a mixture of hydrogen and arsine is then passed directly through a heated glass tube the heat will decompose the arsine into hydrogen. Deposited on the side of the tube is a finely divided arsenic "mirror." By comparing the resulting mirror with mirrors of known quantities of arsenic this property of arsine can serve as a useful test in arsenic determinations.

Arsine reacts with sodium dissolved in liquid ammonia to yield NaAsH_2 . Many compounds analogous to amines can be prepared as a result of this system, Demitras et al., 1972 (87).



In addition, since organic arsenic compounds have been reported to exist in the natural environment, a brief discussion of this chemistry is in order. A great variety of organic arsenic compounds have been synthesized and Table 11 typifies some of the most significant general organic arsenic compounds found in existence. The arsenic atom can bond anywhere from one to five organic groups which can be aromatic and/or aliphatic in nature. If the organic groups do not occupy all the valency positions available to them, other atoms and groups can participate in the bonding. The organic arsenic compounds containing methyl groups are of environmental importance, NAS Report, 1976 (709).

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TABLE 11. SURVEY OF ORGANIC ARSENIC COMPOUNDS

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$RAsX_2$ R_2AsX	$x=H, \text{ halogen, } NR_2, OR, SR, SeR, \text{ alkali metal, pseudohalogen}$
R_3As $(R_4As)^+x^-$ R_5As	Triorganylararsine Tetraorganylarsonium salt ($x=\text{uninegative anion}$) Pentaorganyl arsenic
$(RAsY)_n$ $R_2As-X-AsR_2$	$Y=O, S, NH, NR$ $X=O, S, Se, NR$
R_3AsY R_3AsX_2	$Y=O, S, Se, Te, NR$ $X=\text{halogen}$
$RAsO(OH)_2$ $R_2AsO(OH)$	Organylarsonic acid Diorganylararsinic acid

NAS Report, 1976 (709)

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SECTION 4

GEOCHEMISTRY

The literature search pertaining to arsenic geochemistry has been conducted with the intention of identifying appropriate forms of arsenic for safe containment and elucidating the potential environmental interaction between the various proposed forms of arsenic and the environment of their containment or disposal sites. This review will, then, concentrate upon the geologic occurrence of arsenic, the environmental properties, and processes involving specific forms of arsenic. The argument supporting this direction is that the conceptualization of appropriate models for the safe containment of arsenic should be based upon the chemistry of arsenic in the natural environment, which in turn is reflected by its geologic occurrence.

GEOLOGIC OCCURRENCE

The geologic occurrence has been adequately summarized by Onishi and Sandell, 1954 (203) and by Onishi, 1969 (202), and a relatively recent NAS Report, 1976 (709). What follows here is a brief compilation of that data which is directly related to the objectives of this study as stated above. The geologic occurrence will be subdivided into the data pertaining to the lithosphere and to that of the hydrosphere.

Lithosphere

The data pertaining to the lithosphere will be partitioned into the occurrence of arsenic in various mineral phases, various rock types, and soils and sediments.

Minerals--

Since arsenic is the twentieth most abundant element in the earth's crust and has an average continental crust concentration of 1.5 - 2 ppm, it is not surprising to find that it does not form any common rock-forming minerals and is at low concentration in these phases. The concentrations of arsenic in the rock-forming minerals are relatively lower than its average in the crust. This is illustrated in Table 12. It is of interest to note that compared to the rock-forming minerals, arsenic does appear to have a relatively high concentration in magnetite, ilmenite, e.g., 2.7 - 41, Onishi, 1969 (202).

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TABLE 12. CONCENTRATION OF As IN ROCK-FORMING MINERALS

Mineral	As (ppm) Range	Average
Quartz	0.4 - 1.3	0.85
Feldspar (Potash)	0.7 - 1.7	0.98
Plagioclase	0.8 - 2.1	1.4
Biotite $K(Mg, Fe)_3 AlSi_3O_{10}(OH)_2$	1.4	
Pyroxene $Ca(Mg, Fe, Al)(Al, Si)_2O_6$	0.2, 0.8 0.048 - 0.197	0.074
Amphibole $Ca_2Na(Mg, Fe^{+2})_4(AlFe^{+3}, Ti)_3 Si_6O_{12} 2(O,OH)_2$	1.1, 2.3	
Olivine $(Fe, Mg)_2SiO_4$	0.075 - 0.17	0.11

Onishi, 1969 (202)

Mineral phases in which arsenic is a major constituent are listed in Table 13 along with the observed manner of mineral occurrence. As noted in the NAS Report, 1976 (709), the minerals in Table 13 are just some of the relatively more common ones of the 245 arsenic mineral species. The report states that "Arsenic is found in high concentration in sulfide deposits, where it is present as the native element or alloys (four minerals), arsenides (twenty-seven minerals), sulfides (thirteen minerals), sulfosalts (sulfides of arsenic with metals such as lead, copper, silver, and thallium, sixty-five minerals), and the oxidation products of the foregoing (two oxides, eleven arsenites, 116 arsenates, and seven silicates)." Of these minerals, arsenopyrite is by far the most common. In addition, many sulfides contain appreciable amounts of arsenic in solid solution; the most important of these is pyrite, which has a maximal arsenic content of about five percent (common range, 0.02--0.5%).

Rocks--

The data presented for the concentration of arsenic in various igneous rocks, Onishi, 1969 (202); NAS Report, 1976 (709), and Onishi and Sandell, 1954 (203), indicate that there are no marked differences. Table 14 illustrates typical data.

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TABLE 13. ARSENIC MINERALS

Name	Composition	Manner of occurrence
Arsenic	As	Found in hydrothermal veins
Allemontite	AsSb	Mostly in veins
Algodonite	Cu ₆ As	
Domeykite	Cu ₃ As	
Dimorphite	As ₄ S ₃	
Niccolite	NiAs	Frequently occurs in norites or ore deposits from them. Also found in vein deposits with Co and Ag minerals
Realgar	AsS	Occurs commonly as a minor constituent of certain ore veins associated with orpiment and other As minerals. Also found in certain limestones or dolomites, in clay, and as a volcanic sublimation product or a deposit from hot springs
Orpiment	As ₂ S ₃	Found in hydrothermal veins and as a hot spring deposit, and as a volcanic sublimation product
Sperryllite	PtAs ₂	
Cobaltite	CoAsS	Found in high-temperature deposits and as disseminations in metamorphic rocks
Loellingite	FeAs ₂	Found in mesothermal vein deposits
Safflorite	(Co, Fe)As ₂	Generally in mesothermal vein deposits
Rammelsbergite	NiAs ₂	Commonly in mesothermal vein deposits
Arsenopyrite	FeAsS	The most abundant and widespread As mineral. It occurs in diverse types of deposits, usually as one of the earliest minerals to form
Skutterudite	(Co, Ni)As ₃	Occurs in moderate temperature veins
Proustite	Ag ₃ AsS ₃	Generally one of the late Ag minerals in the sequence of primary deposition
Xanthoconite	Ag ₃ AsS ₃	
Tennantite	(Cu, Fe) ₁₂ As ₄ S ₁₃	Occurs in hydrothermal veins
Enargite	Cu ₃ AsS ₄	Found in vein and replacement deposits formed at moderate temperatures
Seligmannite	PbCuAsS ₃	

(Continued)

TABLE 13. (Continued)

Name	Composition	Manner of occurrence
Smithite	AgAsS_2	A secondary mineral formed by the oxidation of arsenopyrite, native As, and other As minerals
Vrbaite	$\text{TlAs}_2\text{SbS}_5$	
Arsenolite	As_2O_3	
Claudetite	As_2O_3	
Cahnite	$\text{Ca}_2\text{B}(\text{OH})_4(\text{AsO}_4)$	A secondary mineral formed by the oxidation of regular, arsenopyrite, and other As minerals
Berzeliite	$(\text{Mg}, \text{Mn})_2(\text{Ca}, \text{Na})_3(\text{AsO}_4)_3$	
Pharmacolite	$\text{CaH}(\text{AsO}_4)_2 \cdot 2\text{H}_2\text{O}$	
Erythrite	$(\text{Co}, \text{Ni})_3\text{OAsO}_4 \cdot 2 \cdot 8\text{H}_2\text{O}$	
Annabergite	$(\text{Ni}, \text{Co})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	Secondary mineral
Symplectite	$\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$	Secondary mineral
Scorodite	$\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$	Secondary mineral
Hematolite	$(\text{Mn}, \text{Mg})_4\text{AT}(\text{AsO}_4)(\text{OH})_8$	Secondary mineral
Synadelphite	$(\text{Mn}, \text{Mg}, \text{Ca}, \text{Pb})_4(\text{AsO}_4)(\text{OH})_5$	
Adelite	$\text{CaMg}(\text{AsO}_4)(\text{OH}, \text{F})$	
Conichalcite	$\text{CaCu}(\text{AsO}_4)(\text{OH})$	
Austinite	$\text{CaZn}(\text{AsO}_4)(\text{OH})$	Secondary mineral
Durangite	$\text{NaAl}(\text{AsO}_4)\text{F}$	
Tilasite	$\text{CaMg}(\text{AsO}_4)\text{F}$	
Sarkinite	$\text{Mn}_2(\text{AsO}_4)(\text{OH})$	
Olivinite	$\text{Cu}_2(\text{AsO}_4)(\text{OH})$	Secondary mineral
Adamite	$\text{Zn}_2(\text{OH})(\text{AsO}_4)$	
Mimetite	$\text{Pb}_5(\text{AsO}_4, \text{PO}_4)_3\text{Cl}$	
Liroconite	$\text{Cu}_2\text{Al}(\text{AsO}_4)(\text{OH})_4 \cdot \text{H}_2\text{O}$	
Cornwallite	$\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$	Oxidation product of arsenopyrite and other As-rich minerals
Euchroite	$\text{Cu}_2(\text{AsO}_4)(\text{OH}) \cdot \text{H}_2\text{O}$	
Legrandite	$\text{Zn}_4(\text{OH})(\text{AsO}_4)_9 \cdot 12\text{H}_2\text{O}$	
Pharmacosiderite	$\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 5\text{H}_2\text{O}$	
Armangite	$\text{Mn}_3(\text{AsO}_3)_2$	
Finnemanite	$\text{Pb}_5(\text{AsO}_3)_3\text{Cl}$	

Onishi, 1969 (202)

TABLE 14. ARSENIC IN IGNEOUS ROCKS

Rocks	No. Analysis	Arsenic Concentration, ppm. Range Usually Reported	Averages
Ultrabasic	37	9.3 - 16	3.0
Basalts, gabbros	146	0.06 - 113	2.0
Anclesites, clacites	41	0.5 - 5.8	2.0
Granitic	73	0.2 - 13.8	1.5
Silicic volcanic	52	0.2 - 12.2	3.0
Onishi, 1969 (202)			

The data for concentration of arsenic in sedimentary rocks in Table 15 illustrate that there are marked differences between the various rock types. Additionally, it notes that not only is the concentration of arsenic quite variable within one rock type, the average arsenic concentration in sedimentary rocks is much higher than in igneous material.

Soils and Sediments--

Comparatively little information is available on the abundance of arsenic concentrated in the soils and sediments due to the natural weathering of primary and secondary arsenic mineral. Onishi, 1969 (202) reports that various investigators determined the arsenic content of various U.S. soils to be that in Table 16. Onishi reports an approximated average value of 5 - 10 ppm. arsenic.

It would appear that the great percentage of information concerning the arsenic concentration in soils and sediments is that derived from localized studies related to man's activities. Bishop and Chisholm, 1961 (158), measured a total arsenic concentration of 22.4 - 95.3 ppm in soils of an orchard which had been frequently sprayed with lead arsenate insecticide. Crafts and Rosenfels, 1939 (164) reported the variability of arsenic levels in contaminated soils was a function of the soil types. The greatest arsenic concentrations were found in red "heavy" (high iron and clay content) soils and the least concentration in coarse gritty soils having little colloidal matter. This same phenomenon was observed by Dorman et al., 1939 (173) who determined that much less arsenic was lost from clay soil compared to sandy soils. Arnott and Leaf, 1967 (154); Johnson and Hiltbold, 1969 (188); Jones and Hatch, 1945 (189) and Vandecaveye et al., 1936 (217), have all studied arsenic contaminated soils and have observed the arsenic to be in conflict with that of Johnson and Hiltbold, 1969 (188) who state that the arsenic

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TABLE 15. ARSENIC IN SEDIMENTARY ROCKS

Rocks	No. Analysis	Arsenic Concentration, ppm. Range Usually Reported	Averages
Limestones	37	0.1 - 20	1.7
Sandstones	11	0.6 - 120	2.0
Shales & Clays	324	0.3 - 490	14.5
Phosphates	282	0.4 - 188	22.6
Sedimentary Iron Ores	110	1 - 2900	400
Sedimentary Manganese Ores		(up to 1.5%)	
Coal	1150	0 - 2000	13
Onishi, 1969 (202)			

TABLE 16. ARSENIC CONTENT IN U.S. SOILS

% U.S. Soils	Arsenic Concentration (ppm.)
30%	<5
50%	5 - 10
20%	>10 ppm.
Onishi, 1969 (202)	

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seems to be dispersed by leaching in the contaminated soils and that the arsenic is recoverable at depth. This discrepancy appears to be due to variations in soil type as noted by Dorman et al., 1939 (173).

Observations similar to those pertaining to arsenic contaminated soils are those relating to sediments. Sohacki, 1968 (213) reported that arsenic added to the water of a farm pond entered the sediments and that this process reached equilibrium within thirty days. Crecilius, et al., 1974 (167) have reported anomalously high concentrations of arsenic in contaminated Puget Sound sediment samples taken near a copper smelter.

Thus the data emanating from man's activities and that from the natural weathering of arsenic minerals indicate that arsenic is concentrated in the soils and sediments. The information that would be of specific interest to this study, but which appears to be not available, is one that concerns the forms of arsenic in the sediments and soils.

Hydrosphere

There appears to be limited data on the occurrence of arsenic in the surface or ground water system due to the natural weathering of minerals. The great abundance of hydrosphere concentration data has been due to the interest in the pollutant effects of man's activities.

Onishi and Sandell, 1954 (203) report a frequency distribution of arsenic concentration of 0.2 ppm in alkaline and acid hot springs, a 1 ppb value in rain water, and averages ranging from 0.54 to 4.0 ppb in seawater as indicating the approximate values to be found in the uncontaminated hydrosphere. Onishi, 1969 (202) presents a compilation of data from other investigators which is essentially that presented above. Kanamori and Sugawara, 1965 (191) have reported ocean water to have an average 0.6 ug/ml of arsenic and a range of 0.2 to 1.0 ug/liter, and an average of 0.65 ug/ml arsenic and a range of 0.6 to 0.75 ug/liter in antarctica ice. They also reported an average of 1.6 ug/liter of arsenic and a range of 0.01 to 13.9 ug/liter in rainwater in Japan. The higher values in this rainwater were reportedly the result of atmospheric contamination.

ENVIRONMENTAL PROPERTIES AND PROCESSES

Primary Minerals

Although the concentration of arsenic in a magma chamber is probably relatively low, as exemplified by its low concentrations in the earth's crust and in the rock forming minerals, it is of interest to consider the role of arsenic in a crystallizing silicate melt. The ionic radii, oxygen coordination number, and electronegativity of arsenic compared to common rock forming elements, Table 17, indicate that it can probably substitute for Si^{+4} , Al^{+3} , Fe^{+3} , and Ti^{+4} .

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TABLE 17. CO-ORDINATION NUMBER AND ELECTRONEGATIVITY OF ARSENIC AND OTHERS

Ion	Radii (A°)	Oxygen Coordination #	Electronegativity*
As ⁺³	0.58	4,6	
As ⁺⁵	0.46	4	2.0
Si ⁺⁴	0.43	4	1.8
Al ⁺³	0.51	4,6	1.5
Fe ⁺³	0.64	6	1.8
Ti ⁺⁴	0.68	6	1.5

*Pauling Scale

Using Goldschmidt's rules, as described by Mason, 1958 (195), it would appear that the As⁺³ and As⁺⁵ ions would be "camouflaged" in the crystal lattices of aluminum minerals and silicon minerals, respectively. The As⁺³ and As⁺⁵ ions would be "captured" by ferric and titanium minerals, As⁺³ "captured" by silicon minerals and As⁺⁵ "captured" by aluminum minerals.

Additionally, Esson, et al., 1963 (175) have performed a detailed study of the chemistry of a number of rocks of the Skaergaard intrusive series. On the basis of their field data, they have postulated there is a strong tendency for arsenic to concentrate in both interstitial and late stage liquids. They argue that arsenic is probably accepted into octahedral sites usually occupied by Fe⁺³, Mg⁺², Ti⁺⁴ and Al⁺³ and that there is some arsenic substitution for Si⁺⁴ and Al⁺³.

The low concentration of arsenic in the rock forming aluminosilicate minerals is, then, probably not due to any dissimilarity in properties between arsenic and aluminum or silicon, but due to the low concentration of arsenic in the initial stages of magmatic crystallization. The tendency of arsenic to be associated with the iron aluminosilicates would be expected on the basis of the availability of not only octahedral iron and aluminum but also tetrahedral aluminum and silicon sites in the same mineral. This would seem to correlate with the slightly higher concentrations of arsenic in biotite, the pyroxene minerals, and the amphibole minerals. The relatively high concentration of arsenic in the magnetite, titaniferous magnetite, and ilmenite of the Skaergaard intrusives is expected, due to the increase of arsenic concentrations in the late magmatic liquors and the tendency of arsenic to be "captured" by titanium minerals.

Even though the data indicate that arsenic should be captured or camouflaged by the iron aluminosilicate minerals, the abundance of arsenic that is associated with the siderophile and chalcophile elements, Mason, 1958

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(195), i.e., those exhibiting affinity for metallic iron and sulfide, respectively, is relatively large. This indicates that the relatively low concentration of arsenic in the aluminosilicates is explained by the low relative amount of arsenic in the higher oxidation states in the silicate melt. The chemical properties of these low oxidation-state species of arsenic are such that arsenic tends to become concentrated in the late magmatic liquids, which also contain Cu, Ag, Zn, Cd, H, trivalent iron (if of high concentration in the initial magma) and, in addition, sulfur. Thus, even though reduced arsenic does exhibit the tendency to be associated with sulfides, the higher oxidation states of arsenic are chemically similar to Fe^{+3} , Al^{+3} , and Si^{+4} .

It should be noted that the relatively similar concentrations of arsenic in various types of igneous rocks is expected due to the affinity of the higher oxidation states of arsenic for silicon, aluminum and iron and the relatively low amount of oxidized arsenic in the silicate melt.

Secondary Minerals

The marked tendency of arsenic to form arsenates in the natural weathering environment is exhibited by the secondary minerals in Table 13. It should be pointed out that these arsenate phases are the result of the interaction of arsenic with the natural environment. It follows that they are either kinetically stable phases or are actually thermodynamically stable states for specific bulk compositions at earth surface temperatures and pressures.

As discussed by Onishi, 1969 (202) and the NAS Report, 1976 (709), the relative high concentration of arsenic in shales and clays, phosphorites, sedimentary iron and manganese ores and coal is related to either the iron, clay mineral or organic matter content of the sedimentary rock. It has been shown that the arsenic content is not related to the organic content of non-marine carbonaceous and near-shore marine shales; but is related to the carbon content of off-shore marine shales. The relative high arsenic content of phosphorites would appear to be due to the similar chemistry of the AsO_4^{4-} and the PO_4^{4-} ion. Nevertheless, the NAS Report, 1976 (709) reports some successful and unsuccessful attempts to relate the arsenic content of phosphorites to either the organic matter or the iron content.

Soils and Sediments

Although the data available on the processes involving the natural weathering of primary and secondary arsenic minerals in the rocks are essentially nonexistent, Onishi, 1969 (202) reports that it appears the "soils are enriched in arsenic compared to igneous rocks." This same phenomenon was noted above for the sedimentary rocks.

The data noted above pertaining to arsenic concentration in contaminated soils and sediments also clearly indicate that arsenic is concentrated in the soils and sediments. The degree of this concentration is dependent upon the soil type, as reported by Crafts and Rosenfels, 1939, (164) and by Dorman

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et al., 1939 (173). Bishop and Chisholm, 1961 (158) report that the lead arsenate insecticide toxicity is greater in sandy soils than in clay soils. This was concluded on the basis of a water leach of the soil types. These authors also observed that the amount of water soluble arsenic was not related to the total arsenic concentration in the soil, e.g., total As/soluble As: 103.7/0.6; 55.9/10.7; 9.8/0.6. Thus they concluded that the arsenic toxicity is not determined by the total arsenic concentration in the soil, but rather by its solubility. It would, then, appear that the toxicity, i.e., solubility, of the arsenic is influenced by the soil type; clay soils being less toxic than sandy soils. A similar line of evidence concerning the form of arsenic in the soils is the observation by Crecelius et al., 1974 (167). These authors state that most of the arsenic in the contaminated Puget Sound sediments is present in a chemically stable form and postulate that the arsenic is associated with the clay particles. Furthermore, Dickens and Hiltbold, 1967 (172) have studied the adsorption of disodium methanearsanate on various soil types and have concluded the following decreasing order of adsorptive capacity: clay < clay loam < silt loam < loamy sand. Hiltbold, 1974 (181) also observed a strong association of arsenic with clay minerals.

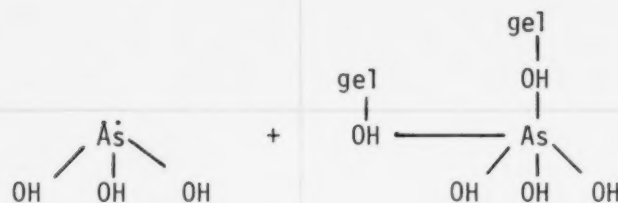
Related to and associated with the role of the clay minerals with respect to arsenic fixation is that pertaining to the role of iron and aluminum content of the soil. Rosenfels and Crafts, 1939 (207) indicate that a high clay content of the soil is usually accompanied by a high iron and aluminum content, and that these heavy soils fix more arsenic than light soils. Hiltbold, 1974 (181) and Tammes and deLint, 1969 (215) state that arsenic in contaminated soils persists if the soils have high iron and aluminum content. Misra and Tiwari, 1963 (199) have observed that the variables having a significant effect upon the fixation of arsenic in soils are the amount of iron and aluminum sesquioxides, amount of calcium, and the soil pH. They postulate that the mechanism of arsenic fixation by the sesquioxide of iron and aluminum could involve a reaction between salts or a salt and a hydrous oxide. Woolson, 1969 (220) also expounded upon the mechanism of arsenic fixation. He stated that the water-soluble arsenic applied to soils is rapidly converted to aluminum-arsenates, which are slowly transformed to iron-arsenates. He notes also that, at high levels of arsenic addition to a soil, more arsenic is fixed by aluminum than iron.

The mechanism of iron sesquioxide fixation of arsenic has been reported by Boswell and Dickson, 1918 (160). They observe that the aqueous trivalent arsenic is strongly adsorbed by ferric hydroxide gel and that the extent of arsenic adsorption is diminished by the addition of NaOH to the system. They postulate the following mechanisms to explain these phenomena of adsorption and NaOH interferences.

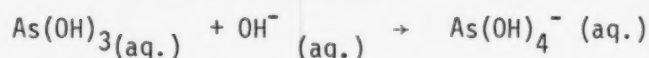
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Arsenic Adsorption Mechanism

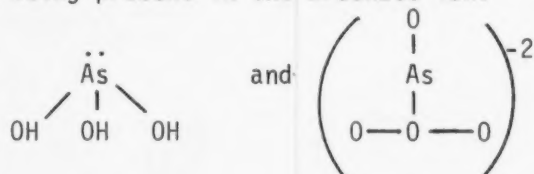


NaOH Interference



Additional justification for the NaOH interference mechanism is, according to Mesmer and Baes, 1974 (708), that Al(OH)_4^- is known to exist in dilute aqueous solutions. Closely associated with these arguments is the observation of Misra and Tiwari, 1963 (199). They reported that as the pH of the aqueous phases increased, the extent of arsenic adsorption in soils decreased. It should be pointed out that this phenomenon is the reverse of that observed for heavy metal adsorption as a function of pH.

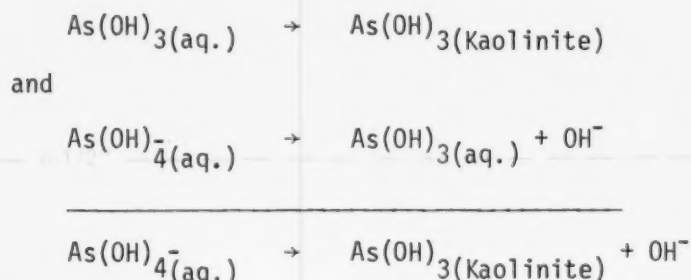
Durrant and Durrant, 1962 (174) state that arsenic prefers a tetrahedral configuration, i.e., exhibits Sp^3 bonding, except when d orbitals are used for trigonal, bipyramidal, and octahedral valence states. These authors further note that arsines and arsenious acid and arsenite, when in tetrahedral configuration, have a lone electron-pair accessible for coordinating with electron-pair acceptors. Roy et al., 1957 (208) have studied the complexing behavior of arsenite with polyhydroxylic organic compounds. They explain the lack of arsenate to form such complexes on the basis of the lone electron-pair not being present in the arsenate ion.



It should be pointed out that the complexation of trivalent arsenic with polyols (organic molecules with many hydroxide groups) is consistent with the mechanism of adsorption of trivalent arsenic with ferric hydroxide gel.

Sieling, 1946 (210) has investigated the adsorption of arsenic on kaolin and has observed an effect of pH. In systems in which the pH was held constant, he observed a decrease in the extent of arsenic adsorption on kaolin with an increase in pH. In an additional experiment, in which the pH was allowed to change as arsenic adsorption on kaolin proceeded, he

observed that the pH increased to a value which remained constant as adsorption continued. Sieling interpreted this as being indicative of anion exchange of arsenic for hydroxides on the kaolin surface. He attributed the attainment of a constant pH to represent the termination of the anion exchange process and the onset of a predominantly molecular sorption process. This postulated mechanism of anion exchange would appear to be incompatible with the argument of arsenic adsorption on ferric hydroxide gel as presented by Boswell and Dickson, 1918 (160) and described above. Again, this mechanism did not indicate a release of gel hydroxide due to adsorption of arsenic. The reduction of aqueous arsenic in the presence of kaolin could be explained by adsorption of the arsenous acid into the lattice site of the octahedral aluminum. The consequent ionization of As(OH)_4^- would account for the increase in pH.



The buffering effect of the polyprotic arsenous acid as the pH increased would result in an eventual constant pH as more arsenic became incorporated into the structure of kaolinite. It should be pointed out that the higher oxidation states of arsenic exhibit chemical properties similar to aluminum and silicon. As described above, arsenic has been shown to be associated with the tetrahedral and octahedral positions of silicon and aluminum in aluminosilicate minerals crystallizing from a magma.

Another complication with respect to the fixation of arsenic in a soil is the role of soil calcium. Johnson and Hiltbold, 1969 (188), Woolson, 1969 (220), Woolson, et al., 1971 (222), and Woolson and Kearney, 1973 (223) have shown that the adsorption of arsenic decreases not only as the pH increases but also as the calcium in the soil increases. This was interpreted as indicating that arsenate reacts with calcium to "form slightly more soluble calcium arsenates." This is a confusing interpretation in light of the general observation that the more insoluble precipitates will form at the expense of the more soluble ones. Additionally, Page, 1974 (710) and Woolson et al., 1971 (222), state that when the exchangeable calcium levels in the soil are low, arsenic is more likely to leach.

Hopke et al., 1976 (183) have investigated the geochemical profiles of arsenic in the sediments of Chautauqua Lake. This lake has had a history of being sprayed with sodium arsenite. The sediment clay minerals are predominantly illite, chlorite and some mixed layer minerals. These investigators observed a positive correlation coefficient with the clay mineral and

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the organic matter concentration of the sediments. A conflicting result is reported by Jacobs et al., 1970 (185). They observe that arsenic is not adsorbed by humic material, which is unlike that observed for heavy metals. As noted earlier, there has been some contradictory evidence concerning whether or not arsenic is related to the organic content of phosphorite rocks. It should be pointed out that the lack of similarity in the adsorptive characteristic of arsenic and the heavy metals is not surprising when it is recalled that arsenic is present in aqueous solution as an oxy-anion.

Aqueous Systems

The investigations of interest pertaining to arsenic in the hydrosphere are those concerned with elucidating the form of arsenic in the natural aqueous phase and the processes associated with its concentration control.

Onishi and Sandell, 1954 (203) experimentally observed that the oxidation states of arsenic in the oceanic system range from 69 to 100% pentavalent states. Penrose, 1974 (204) reported that under normal pH and pO_2 , inorganic arsenic should exist in seawater entirely as the pentavalent state--but this has not been observed. Johnson, 1972 (187) reported that marine bacteria reduce arsenic from the pentavalent to the trivalent states. They observed that the pentavalent-trivalent ratio was a balance between chemical oxidation and biological reduction. A further complication to the aqueous form of arsenic is the observation of Ferguson and Gavis, 1972 (176) that the rate of oxidation of trivalent to pentavalent arsenic in the aqueous phase is very slow at neutral pH values.

Crecelius, 1975 (165) investigated the fate of smelter arsenic contamination in the water and sediments of Lake Washington. They experimentally determined the forms of arsenic in various components of this system, Table 18.

TABLE 18. FORMS OF ARSENIC CONTAMINATION

Chemical Form	System
As ₂ O ₃	Smelter dust
80% arsenite +pH 5.5	Smelter dust plus distilled water
*35% arsenite	Rain
40% arsenite	Lake water
60% arsenate	
55% arsenite Small % dimethylarsenic acid	Sediment interstitial water
*There is a suspicion that some of the arsenite may have oxidized in the rain catcher.	

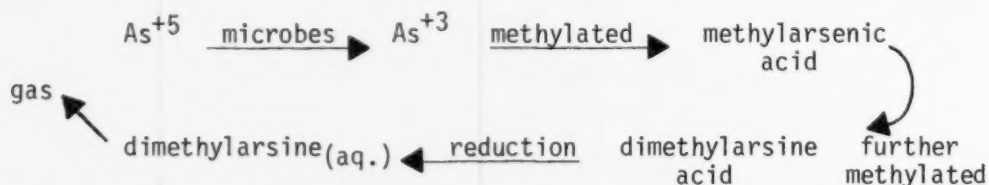
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Kanamori, 1965 (190) explained the observed stratification and sedimentation of arsenic in a lake. They experimentally determined that arsenic is coprecipitated with ferric hydroxide under oxidative conditions and low concentration of arsenic. In brackish water the arsenic is separated from the iron due to the precipitation of iron as a sulfide. These experimental results were verified with observations of arsenic in the lake sediment and by solubility calculations. Skripach et al., 1970 (211) have reported the removal of both +5 and +3 arsenic from waste water streams with iron salts in combination with calcium hydroxide. They observed the removal efficiency of arsenic to increase with the increase in iron concentration. The required Fe/As ratio was 5/1 for complete removal of the +5 state and 10/1 for the +3 state. If there is not enough iron present in the aqueous system, the system had to be agitated at pH 8-10 in order to oxidize the trivalent arsenic. Keaton and Kardos, 1940 (193) had reported the same required ratios of Fe/As and explained the 10/1 Fe/As was due to the triavalent iron oxidizing triavalent arsenic to pentavalent arsenic.

Other methods have been illustrated as being effective for the removal of arsenic from an aqueous system. Nilsson, 1971 (200) reported calcium hydroxide effective in removing pentavalent arsenic from contaminated water. Ross, 1973 (711) postulated that arsenic is removed by precipitation as either oxides and hydroxides or is adsorbed on various minerals. Ross states that the principal natural mechanism is the dilution of the contaminated waste streams by runoff or rain, which raises the pH and causes arsenic to precipitate as a hydroxide. Bellack, 1971 (156) has shown that alum flocculation followed by filtration through activated alumina is an effective technique for arsenic removal. Finally, Angino et al., 1970 (153) reported that 85 percent of 200 ppb arsenic in an aqueous solution is removed by a cold-lime softening treatment and 70 percent by charcoal filtration.

A final point should be made concerning the behavior of arsenic in the aquatic and/or sediment environments. The arsenic removed from the aqueous phase and placed in aquatic sediments cannot be considered to be permanently removed due to aerobic microorganisms transforming the arsenic into volatile methylated arsines. McBride and Wolfe, 1971 (196) have deduced the following mechanism describing the geochemical cycle of arsenic in a natural aqueous system.



Similarly, Ferguson and Gavis, 1972 (176) have proposed that reduced forms of arsenic are oxidized to arsenate in the aerobic water of a lake and that the arsenate is coprecipitated with ferric hydroxide. A part of the precipitated arsenate is distributed to low-oxygen portions of the lake where it is

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reduced to HAsO_2 and AsS_2^- . Microbes then methylate the arsenic or further reduce it to arsine. These reduced or methylated forms release arsenic back into the lakewater. The mechanisms as proposed by Ferguson and Gavis, 1972 (176) are presented in Figure 7.

These arguments concerning the geochemical cycle of arsenic illustrate the close relationship between the properties and processes involving arsenic in the aqueous systems, and in the soils and sediments. Research by Griffin et al., 1976 (705) on the effect of clay minerals used as liners for waste disposal sites directly relates to this question, i.e., the interaction of arsenic between the aqueous and sediment phases. As noted earlier by Misra and Tiwari, 1963 (199), the adsorption of the heavy metals increased with increase in pH whereas that for the anionic heavy metals, such as Cr^{+6} , As and Se, decreased. Griffin concluded that the "removal of the heavy-metal anions is primarily an anion-adsorption reaction in which the monovalent ion is the one being predominantly adsorbed." This was the result of observing that the experimental maximum in arsenic adsorption occurs at the same pH that H_2AsO_4^- species is at maximum concentration. In fact, the arsenic adsorption curves were observed to closely follow the pH-concentration curve for H_2AsO_4^- .

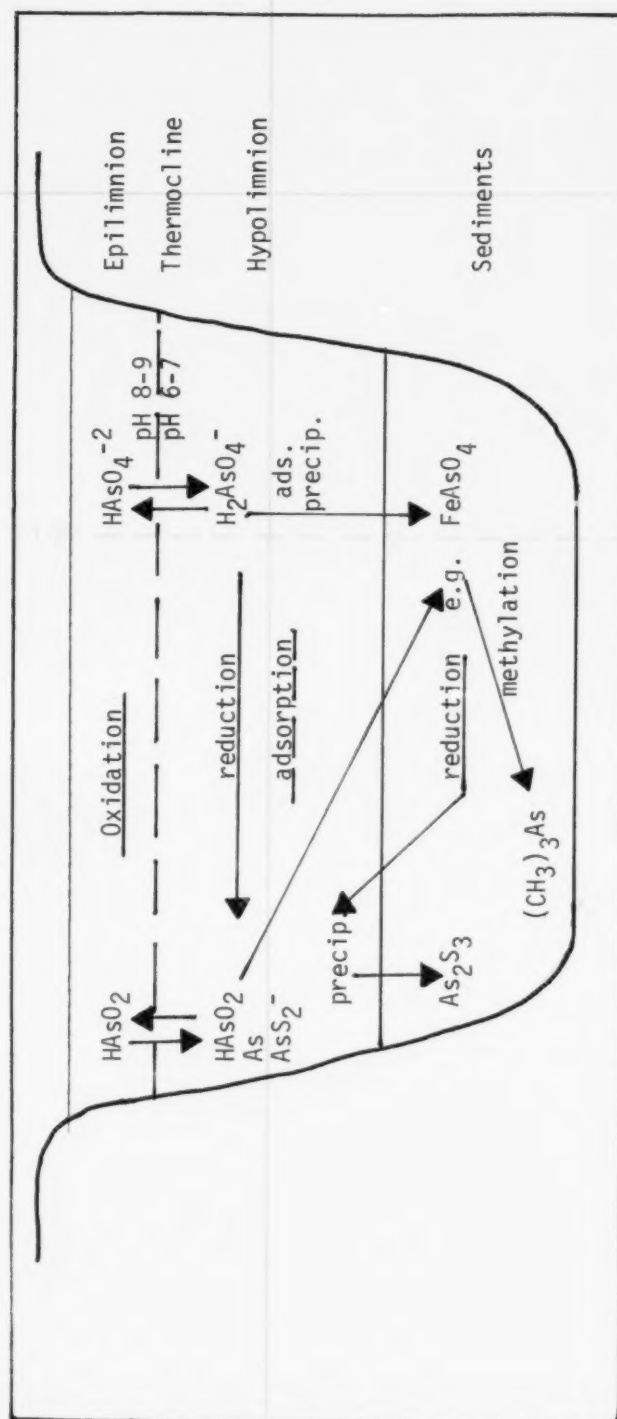
The interaction of such soils containing arsenic clays with an aqueous environment essentially free of arsenic is of great interest to considerations of the safe containment or disposal of arsenic. Korto et al., 1976 (706) have investigated the leaching characteristics of the same soils that were used in the adsorption experiments noted above by Griffin et al., 1976 (705). These soils containing various clay minerals with adsorbed arsenic, and other heavy metals, were leached with 0.1N HCl and water. These data are compiled in Table 19.

It should be pointed out that the leached arsenic (as well as other metals) came from the top of the soil columns. Therefore, it would appear that the metals were quantitatively adsorbed within the top of the soil column and under natural conditions would migrate downward as they are leached.

Additional information concerning the removal of arsenic from an aqueous phase is reviewed in the section of this report entitled Waste Water Treatment.

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Ferguson, J.E., and J. Gavis, "A Review of the Arsenic Cycle in Natural Waters." Water Research 6:1259-1274, 1972. Reprinted with permission of Pergamon Press, Ltd.; Elmsford, New York.

Figure 7. Local geochemical cycle for arsenic

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TABLE 19. COMPILATION OF ARSENIC LEACH DATA

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Predominate Soil Clay Mineral	Soil pH	Soil Fractions			% Free Iron Oxides	Amount of Sorbed As Leached 0.1NHC1	
		% Sand	% Silt	% Clay		H ₂ O	
Kaolinite Chlorite	4.2	88	8	4	0.6	11	0
Vermiculite Kaolinite	4.5	10	60	31	4.0	11	3
Chlorite Kaolinite	4.7	91	4	5	1.8	18	2.5
Kaolinite	6.2	19	20	61	17.0	5	0.5
Kaolinite Gibbsite	6.2	23	25	52	23.0	0	0
Montmorillonite Vermiculite	6.6	7	58	35	3.1	?	?
Vermiculite	6.7	3	47	49	5.6	11	2
Montmorillonite Mica	7.0	35	19	46	3.7	24	4.5
Mica Kaolinite	7.3	52	37	11	1.7	11	0
Mica Montmorillonite	7.8	32	28	40	2.5	20	11.5
Montmorillonite Mica	7.8	71	14	15	1.8	13	0

Korto, et al., 1976 (706)

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SECTION 5

PROCESSING TECHNOLOGY

A large number of literature articles are available that cover the removal, retention, or extraction of arsenic during the industrial processing of ores. Sometimes the processing treatments are designed to remove arsenic, but most often arsenic is removed as a consequence of the treatment process. In either case, arsenic is transformed and/or transported during particular unit operations. The discussions in this section are presented to summarize the literature in three broad categories: Pyrometallurgical Processes, Hydrometallurgical Processes, and Other Processes. Further subdivisions are made according to the common unit operations used in industry.

PYROMETALLURGICAL PROCESSES

Elevated temperature treatment processes are termed pyrometallurgical processes. The unit operations of roasting and smelting are treatment stages used in many metal recovery sequences. The following discussion of the arsenic literature will be subdivided according to these unit operations headings.

Roasting Processes

The roasting of ores, concentrates, flue dusts, etc., is discussed below under the headings, oxidation roasting, reduction roasting, sulfation roasting, and chlorination roasting.

Oxidation Roasting--

The roasting of sulfides to oxides in an oxidizing atmosphere can result in a) the removal, by volatilization, of a large fraction of the arsenic as arseneous oxide, As_2O_3 or b) the complete retention of arsenic by controlling the roast parameters to form iron or alkaline earth arsenates.

Arseneous oxide is a volatile compound, i.e., its boiling point is in the range 457-465°C. It sublimes readily at temperatures well below its boiling point, i.e., its vapor pressure at 260°C is approximately 16 torr, NAS Report, 1976 (709). Experimental conditions that favor its formation therefore, result in its effective removal. Examples of oxidation roasting techniques quoted in the literature are presented below.

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Arsenic can be removed from pyrite concentrates, according to Fassina and Fassina, 1951 (231), by heating to 400°C in a stream of air (see also Wolf, 1968 (263)). Arsenic is evolved as the gaseous oxide.

The treatment of flue dusts from copper smelter operations are described by Hayward, 1952 (28). The description is of past, not present, practice at the Anaconda Smelter in Anaconda, Montana for the production of As_2O_3 . A product containing 93-95 percent As_2O_3 was produced.

The only facility at present in the United States treating flue dust for arsenic extraction is the American Smelting and Refining Company (AS&R) smelter at Tacoma, Washington. Their process is described in a general way in a recent publication by the National Academy of Science; NAS Report, 1976 (709) and in a profile report on the disposal of hazardous wastes; EPA, 1973 (701).

The process used at AS&R is very similar to the process described by Hayward quoted above. As_2O_3 is volatilized from the dust or ore in multi-hearth roasters. The gases containing As_2O_3 pass into condensing chambers. This crude As_2O_3 is recovered and purified by reheating in a reverberatory furnace at 500°C. The As_2O_3 volatilized is carried through a flue system to condensing chambers. The product contains 93-95 percent As_2O_3 .

In the past, there were a few arsenic smelters that manufactured As_2O_3 from the arsenic ores of pyrite and arsenopyrite types. The ores were concentrated and roasted either in rotary kilns or hearth-type roasters. The fumes were passed through a dust collector and then to a cottrell precipitator. The unrefined product ranged from 85 to 98 percent arsenic, Doremus, 1919 (227); Young, 1924 (264); U.S. Patent, 1908 (260); U.S. Patent, 1919 (238), and Anon., 1911 (230).

Other processes for making white arsenic (As_2O_3) from cottrell plant dust and blast furnace dust are also described, Williams, 1920 (262) and Elton, 1925 (229). These dusts were charged in a reverberatory furnace connected to cooling chambers. The sublimates were cooled here and then resublimed giving refined As_2O_3 . Grenier, 1950 (22) has described a process of wet refining crude As_2O_3 by leaching with hot water or NH_4OH with subsequent precipitation. Production of crystalline arsenic can be made from As_2O_3 ; Ger. Offen., 1969 (236), e.g., As_2O_3 when suspended in NH_3 gas stream decomposes NH_3 catalytically at 700°C and liberates hydrogen. The hydrogen reduces the As_2O_3 to metallic arsenic. This is a continuous process.

As noted earlier it is possible to retain essentially all the arsenic as solid compounds by oxidation roasting. This occurs when the conditions are favorable for the formation of iron arsenates and alkaline earth arsenates. Examples of treatments quoted in the literature for this type occurrence are discussed below.

Fluidized bed roasting of arsenopyrites was studied by Vian et al., 1963 (259). They showed experimentally that arsenic could be fixed in the

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calcines by oxidation roasting. The critical parameter is oxygen partial pressure. The temperature range investigated was 720° - 800°C. If the quantity of air used exceeded approximately 90% excess of the stoichimetric requirement of air then arsenic was retained in the calcine as iron arsenate. If the air content was controlled at lower levels, the formation of iron arsenate was thermodynamically unfavorable and arsenic has volatilized as As_2O_3 . The authors present a thermodynamic argument in support of their experimental results. They also use their thermodynamic model to interpret similar experimental studies (using different air/pyrite ratios) on arsenopyrites by Görling and Appler, 1959 (234) and Heath and Holle, 1957 (235).

Several studies are reported on oxidation roasting of Kerch (Russian ore deposit) iron ores: Vasyutiniskii, 1961 (253), 1963 (254), 1964 (255), 1965 (256), 1968 (257) and Tatsiyenko, 1968 (250). Kerch ores were subjected to oxidizing roasts at 800°-1000°C. Volatile arsenic oxide formed and reacted with clay constituents such as dolomite, gypsum, alumina gel, silica gel. The most effective agents were shown to be gypsum, other calcium compounds, alumina silicates, and alumina gel at about 900°C. The arsenic containing clay material could then be separated from the magnetite by magnetic separation. Magnetic separation, of course, is only successful for magnetic, iron oxides, Fe_3O_4 . Those containing hematite, Fe_2O_3 , must be treated by reduction roasting techniques to convert the hematite to magnetite and at the same time to free the arsenic from its arsenates. Reduction techniques are covered in the following section on reduction roasting processes.

Lead smelter flue dusts, Aidarova, 1960 (224), when roasted with lime also retained the arsenic as a calcium arsenate. Similar results were obtained on lead concentrates and lead flue dusts by Oldright, 1934 (247). Conditions can be specified, however, to decompose the arsenates with release of arsenic oxide.

Treatment of gold-arsenic-iron concentrates was studied by Kolesnikov, 1967 (241); Reingol'd, 1969 (249); Zhuchkov, 1968 (255); and Bolidens Gruvaktiebolag Patent, 1966 (226). Their results are in accord with the conclusions of Vian, i.e., arsenic can be effectively removed from the solids or may be retained in the solids depending on the experimental parameters chosen.

Another type of oxidizing roast in the presence of sodium compounds produces a solid product containing arsenic as a water soluble compound, Na_3AsO_4 . The arsenic can therefore be removed from the roasted solid mixture by water leaching, Alekseev, 1966 (225); Matsunaga, 1963 (245), (246); Trifonoff, 1911 (252); Paschen, 1968 (248); Fedotova, 1969 (232); Instituto Nacional de industria Patent, 1960 (237) and Eddy, 1931 (228).

Reduction Roasting--

Roasting in a reducing atmosphere can be very effective in volatilizing arsenic. The effect of a reducing atmosphere is to decompose the arsenate compounds. This allows the arsenic to either volatilize as arsenic metal or

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arsenic oxide. The reducing agent can be carbon, carbon monoxide, or hydrogen. Several reduction roasting processes are described in the literature.

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Schwarz, 1969 (294) describes a process for treating iron ores for arsenic removal. Effective arsenic evolution was produced in rotary kilns, fluidized beds, and traveling grate roasters. The reducing agents used were CO, H₂ and coal over a temperature range of 800-1000°C. Even ores treated by an oxidizing roast containing up to 14% limestone flux (calcium arsenate was formed) could be effectively lowered in arsenic by the reduction roast treatment. Similar results are reported by Karoleva, 1971 (280).

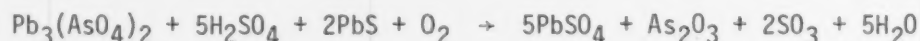
Reduction roast results on Kerch hematite iron ores, sometimes called magnetizing roast because non-magnetic hematite is converted to magnetic magnetite, are reported by several investigators: Grebnev, 1957 (272), 1959 (273); Gerasimov, 1958 (233); Pokhvisnev, 1961 (292), 1962 (293); Yurov, 1963 (300); Kovtun, 1964 (283); Yadryshnikov, 1964 (298); Kratochvil, 1964 (284); Vastyutinskii, 1974 (297). Arsenic is volatilized as the oxide or under proper conditions it is preferentially reacted with the clay components of the ore. The arsenic containing compounds can be subsequently removed by physical concentrating techniques. Elimination of up to 80 percent of the arsenic seems possible.

Grillo et al., 1964 (274); Loskutov, 1962 (286); Triandaf, 1964 (296); Oprea, 1969 (290); Chernyavskaya, 1963 (268); Lakernik, 1959 (243); Kochnev, 1964 (282) have also described reduction roasting processes for the removal of arsenic for mainly nonferrous ores and for dusts produced during the smelting of such nonferrous ores.

Other patents and articles on miscellaneous ores, concentrates, or dusts by the treatment of reduction roasting procedures not listed above are included in the bibliography.

Sulfation Roasting--

Sulfation roasting is a common technique used to solubilize some metallic elements, i.e., to produce water or dilute sulfuric acid soluble metal sulfates. It can be effective in arsenic removal because the arsenates are sulfated thereby releasing the arsenic to the gas phase as the trioxide, e.g., sulfated lead containing flue dusts to produce As₂O₃, Getskin, 1959 (307), 1962 (308), 1961 (309).



Sulfation of metallurgical dusts has been reported by several investigators. Acid pugging and subsequent roasting in air or oxygen enriched air seems to be a common approach taken in several studies, e.g., Michels, 1958 (313) treated dust from pyrite roasting with sulfuric acid and pyrite then roasted in air at 500°C. Iron oxide and volatile arsenic oxide were produced.

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Acid pugging has also been applied to nonferrous types of flue dust. Copper flue dusts were studied by Sosnovskii, 1961 (321). The dust was granulated using H_2SO_4 acid. These granules when roasted at $300^\circ C$ resulted in sulfation of the Pb, Cd, and Zn. Eighty-five percent of the arsenic was evolved. Also flue dusts from nickel concentrate roasting, Shaefer, 1964 (316), when pugged with acid and heated to $600^\circ C$ resulted in effective arsenic removal, i.e., a flue dust containing thirty percent As was lowered to 0.9 percent As by this treatment. Galimov, 1961 (305) treated copper smelter dust by granulating with sulfuric acid, roasting in the presence of coke in a fluidized bed. He achieved 90% arsenic removal.

Other examples are given by Getskin, 1959 (307) for treating lead bearing flue dust and Davydov, 1967 (303) for treating copper converter dusts. Both treatments require sulfation in concentrated sulfuric acid with subsequent roasting at $350-400^\circ C$ for arsenic volatilization as the trioxide.

Chlorination Roasting--

Many metals form volatile chlorides at low temperatures. The chlorinating agent may be chlorine gas, hydrogen chloride gas, or chloride compounds, e.g., NaCl or $CaCl_2$. Sometimes, for the more stable compounds, reducing agents are also necessary, e.g., C or CO.

By controlling the operating parameters, arsenic can be separated as a volatile chloride compound or it can be retained in the solid residue.

Several experimental studies on arsenic removal by volatilization are reported in the literature. Both chlorination and reduction-chlorination studies are reviewed.

A variety of arsenic containing solids have been treated to remove the arsenic by chlorination techniques, e.g., flue dusts, ores, concentrates, slags, slime, and smelter by-products. Examples are presented below.

Techniques for treating iron pyrite and iron pyrite calcines are described by Okubo, 1968 (359); Orie, 1970 (360); Colombo, 1968 (334); Kunda, 1969 (351); Walker, 1939 (325); Dumitru, 1973 (341); Pajak, 1965 (361); Johannsen, 1958 (278); and Mazanek, 1957 (354). Most of these studies involve the reduction-chlorination procedure using coal, coke, or coke oven gas as the reducing agent, and calcium chloride as the chlorinating agent. Temperatures used varied but were in general relatively high, i.e., $700^\circ C-1200^\circ C$.

Treatment of nonferrous concentrates, residues, dusts, etc., have been studied by a number of investigators. The techniques used are similar in concept to the treatment of iron pyrite but are normally performed at lower temperatures, i.e., $< 600^\circ C$. Examples are quoted below. Most of the processes are reduction-chlorination based treatments.

Treatment of zinc leach residues are described by Roeder, 1969 (362); electrolytic copper refining slimes by Mellgren, 1966 (355) and Hoffman, 1965 (328); nickel matte by Sridhar, 1974 (366); Bell, 1975 (330) and

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Babachanov, 1966 (329); lead smelting slags by Hruby, 1958 (345); copper foundry cottrell dust by Slobodska, 1935 (364); zinc drosses by Gray, 1963 (331); cobalt-nickel ores by Haddan, 1922 (344); polymetal sulfide ores by Chizhikov, 1934 (333); and arsenic-cobalt ores by Denisov, 1960 (336).

If desired, it is possible to keep the arsenic in the solids instead of volatilizing it off as a chloride. Engel et al., 1958 (342) developed such a technique for lead ores. The ore was roasted at 1000°C with CaCl_2 in an oxidizing atmosphere. Lead, gold and silver were volatilized but 94% of the arsenic was retained. Shigematsu, 1968 (363) retained the arsenic in iron sulfide while volatilizing other metals such as copper, lead and zinc. Mazanek, 1960 (353) found that arsenic retention in iron ores increased as the CaO content increased.

In addition to the broad classes of roasting discussed above, it is pyrometallurgically possible to evolve volatile sulfide compounds from sulfide ores or concentrates. Arsenic sulfide is volatile at low temperatures and may be effectively removed in the sulfide form under some carefully controlled conditions, e.g., sintering of zinc blende, Metallgesellschaft Patent, 1951 (356) and International Mining Trust Patent, 1935 (347).

Another volatilizing technique that is possible, but much too expensive, is vacuum roasting of arsenic bearing ores, e.g., Voigt, 1953 (337) and Isakova, 1965 (348).

Other suggested treatments are listed in the bibliography but are not reviewed here.

Smelting Processes--

The literature review is not considered to be comprehensive and all inclusive with respect to arsenic removal practices during smelting operations. Every pyrometallurgical process that is used to treat arsenic containing ores and concentrates produces arsenic containing byproducts in some form or another. To include every article on current and past smelting practices would not add significantly to the information desired for the present project.

However, if the reader desires to acquire a general knowledge of the pyrometallurgical sequence of processing stages for copper, nickel, lead and zinc production, then the following references are recommended: Hayward, 1957 (28); Pehlke, 1973 (381); Rosenqvist, 1974 (384); EPA Report, 1974 (702); Dasher, 1976 (370); and Yannopoulos, 1976 (389).

Several literature references are included in the bibliography as examples of arsenic elimination processes. Also other examples are included in the section on general roasting.

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HYDROMETALLURGICAL PROCESSES

A large amount of literature exists that presents proposals and discusses experimental studies on the removal of arsenic from various solid ores, concentrates and industrial by-products (both solids and liquids). A summary of a portion of this literature is presented below. The material is divided into two main categories, Leaching and Solution Purification. Each category is further sub-divided as follows: Leaching: Arsenic Containing Ores, Industrial Dusts, Miscellaneous Industrial By-Products; Solution Purification: Precipitation, Solvent Extraction, Ion Exchange, and Volatilization.

Leaching

Arsenic Containing Ores--

A variety of arsenic containing ores have been subjected to basic sodium sulfide leach solutions. Results are reported below.

Extraction of arsenic by basic solutions containing sodium sulfide at atmospheric pressure results in variable, 30 - 98%, arsenic dissolution; Ivkovic, 1955 (420) found that antimony-arsenic sulfides leached readily in Na_2S solutions, 98% extraction. Holmes, 1973 (419) reports excellent arsenic extraction from copper sulfide concentrates. Agladze, 1957 (411) reports 98% extraction of arsenic from arsenic sulfide ores. Other studies report low arsenic extraction, 30 - 60%, for antimony-arsenic sulfide ores, Agladze, 1960 (410), 1957 (412).

Autoclave leaching, i.e., elevated pressure processes, by basic sodium sulfide solutions is very successful for arsenic extraction. Khryashchev, 1969 (424), (425), 1968 (427) reported 97.5% As extraction from sulfide gold arsenic concentrates. Jangg, 1958 (422), 1959 (423) reported 90 - 100% As extraction. Arsenopyrite was autoclave leached by Plaksin, 1959 (433). He achieved 98 - 99% arsenic extraction.

Autoclave leaching of arsenic containing ores or concentrates can also be accomplished using reagents other than sodium sulfide solutions. Complex sulfide concentrates were autoclave leached in sulfuric acid by Turchaninov, 1963 (437). The arsenic remained in the solids as iron arsenate. Cobalt-arsenic ores, Dobrokhotoy, 1961 (418), when autoclave leached in ammonium carbonate yielded 80% extraction.

Leaching cobalt-nickel ores at atmospheric pressure in a basic solution of NaOH yields arsenic extraction values of 88 - 90%, Nikolaev, 1965 (430), (431). Bacterial activity can result in increased arsenic extraction rate from sulfide concentrates subjected leaching, e.g., Pol'kin, 1970 (434); Ehrlich, 1964 (419); and Kulebakin, 1971 (428).

Industrial Dusts--

Arsenic containing industrial dusts are often produced during the

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pyrometallurgical treatment of sulfide ores and concentrates. Treatment techniques vary greatly depending on the form of the arsenic, i.e., whether oxide, sulfide, or arsenates.

Arsenous oxide is soluble in water. Therefore, if the predominant arsenic specie present is as this oxide, water leaching should be effective. Studies have shown water leaching to be a feasible technique only for a few selected dusts. Lovchikov, 1959 (447) described the treatment of secondary dust from a tin plant. The dust contained 33.4% As as As_2O_3 . It was leached with water at 95°C. Ninety-three percent of the As was extracted. Shul'gin, 1967 (461) reported that lead converter flue dusts are treated with water to partially extract arsenic. Further treatments are necessary because not all the arsenic is present as As_2O_3 .

Sodium sulfide basic solutions are very effective for extracting arsenic from flue dusts. Atmospheric leaching at elevated temperatures, 80°C - 95°C, appears to be effective for a variety of flue dusts. This is contrasted to the need for autoclave leaching for ores and concentrates discussed earlier.

Effective arsenic extraction by basic leach solutions is reported by Polyvyannyi, 1964 (454), 1962 (452), 1961 (451), 1962 (455), 1963 (453), 1961 (456); Ponomarev, 1957 (457); Gnalyshenko, 1961 (443); Auezov, 1963 (439); Polynbetova, 1963 (450); Knoepke, 1974 (445); and Bogdanov, 1972 (440).

Success in extracting arsenic from dusts by acid leaching has also been reported: Knoepke, 1974 (445); Serikov, 1960 (450); Tanaka, 1955 (462), 1955 (463); Illig, 1951 (464); and Schopper, 1934 (449).

A commercial process used by Dowa Mining Company at their plant in Kosaka, Japan is described by Mohri and Yameda, 1976 (448). Flue dust is leached in sulfuric acid, valuable metals recovered, and arsenic precipitated as iron arsenate and subsequently disposed of in a tailings pond. A flowsheet, visualized from the literature, is presented in Figure 8.

Industrial By-Products--

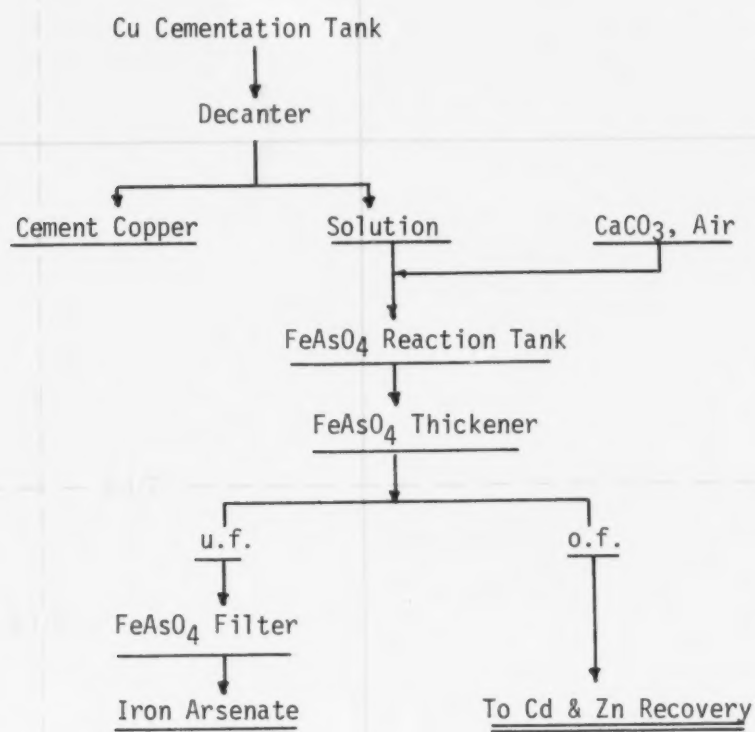
Treatment of industrial by-products produced during pyrometallurgical, hydrometallurgical and electrometallurgical treatments not covered under the previous leaching headings are summarized here.

Speiss is an arsenic-sulfur-metal mixture formed during pyrometallurgical smelting operations. It can be treated hydrometallurgically for metal recovery and arsenic separation.

Sulfuric acid autoclave leaching of speiss is reported by Gerlach, 1963 (434). Speiss can be completely dissolved in two hours at 140°C and 15 atmospheres of oxygen. The arsenic can be separated from solution by precipitation with ferric iron or lime. Khryashchev, 1967 (494), 1965 (480), (481) studied the autoclave leaching of speiss in basic sodium hydroxide solutions. Greater than 98% arsenic extraction was achieved under proper

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operating conditions.

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Treatment of other miscellaneous by-products for arsenic extraction has been reported. Anode slimes from electrolytic copper cells can be acid pugged, low temperature roasted and water leached. Arsenic is then precipitated from solution as an iron or calcium arsenate, Hanske, 1968 (471); Savin, 1965 (493). Arsenious cake from refining of cadmium solutions can be sintered with sodium carbonate at 600°C, then water leached to yield greater than 95% of the arsenic, Kabanova, 1960 (477). Similar processing techniques are described for lead filter cakes by Snurnifov, 1965 (495), i.e., a low temperature roast is performed with a sodium containing compound. A water soluble sodium arsenate is produced.

Solution Purification

Precipitation--

Many processing techniques exist for removing arsenic from solution but most are based on precipitation as an arsenate compound.

Lime is the most common precipitating agent. Calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$ is formed. The optimum temperature, pH, lime/arsenic ratio depend somewhat on the solution being treated. Experimental results are presented by Schopper, 1924 (572); Bassett, 1925 (502), 1926 (503); Schleicher, 1926 (571); Fester, 1933 (516), 1946 (517); Pearce, 1936 (553), 1937 (552); Voight, 1939 (588); Sanfourche, 1951 (568); Pickering, 1907 (556); Dachzelt, 1955 (511); Polyvyannyi, 1963 (561); Plotnikiv, 1964 (559); Tsyb, 1967 (587); Buzur-Ool, 1968 (509); Nikilaev, 1970 (550); Petrosyants, 1971 (554); Pol'kin, 1972 (560) and Dimitrova, 1974 (514). Also, many of the papers on leaching, discussed in previous sections, describe solution purification by lime neutralization and calcium arsenate precipitation.

Iron arsenate is the second most quoted form of precipitated arsenic recovered from leach solutions. Iron is readily extracted in many hydro-metallurgical treatment processes. It can be precipitated from solution by a two-step process, i.e., oxidation of the ferrous ions to the ferric form and then neutralization to precipitate the iron as ferric hydroxides, or jarosite (a sodium, potassium, or ammonium iron hydroxide sulfate compound, $(\text{Na}, \text{K}, \text{NH}_4) \text{Fe}_3(\text{SO}_4)_2 (\text{OH})_6$). If arsenic is present in solution it will precipitate with the iron compounds as ferric arsenate. Experimental techniques and results are presented by Ivanova, 1969 (528); Kaloc, 1967 (533); Enzfelder, 1953 (515); Junghanss, 1975 (530); Pitzer, 1934 (558); Rodzaevskii, 1961 (567); Kabanova, 1957 (531), and Ikebe, 1931 (526).

Precipitation of lead arsenates is described by Riches, 1919 (566); Mitchell, 1926 (547); Lihme, 1919 (543); Merrimac chemical Company, 1918 (545), (546); and Gagnon, 1941 (519). Precipitation of titanium arsenate is described by Hollo, 1968 (525). Ninety-eight percent extraction was achieved.

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Precipitation of many arsenates is possible by proper control of the solution pH. The solubility of many arsenates; Fe^{++} , Fe^{++} , Cu^{++} , Co^{++} , Mn^{++} , Zn^{++} , Ni^{++} , Ca^{++} ; as a function of pH is presented by Gerlach, 1963 (522). By proper pH control one arsenate can be precipitated in preference to another. Also the solubility of an arsenate can be controlled by storing it in a solution that has a properly controlled pH.

Precipitation of arsenic from a solution as an oxide is not as successful as co-precipitation and adsorption on an associated oxide or hydroxide. Effective arsenic removal from water-arsenic solutions by co-precipitation has been demonstrated by Nikolaev and Mazurova, 1970 (550); Portman, 1964 (127); Plotnikov and Usatova, 1964 (559). The stability to subsequent leaching during storage of the solid residues produced by this technique is presently unknown.

The presence of arsenic in solutions that contain copper or zinc is undesirable. It has a detrimental effect on the recovery of these metals from solution by electrolysis. The arsenic may be removed from the electrolyte solution by either electrodeposition as an arsenic sludge or it may be precipitated as calcium or sodium arsenate.

In electrefining of copper, the impure copper anodes, containing arsenic as well as other impurities, are electrolyzed in a suitable bath of acid electrolyte consisting of an aqueous solution of sulfuric acid and copper sulfate. When current flows from the anode to the cathode, the copper in the anode dissolves and is deposited as high purity copper on the cathode. Impurities dissolve in the electrolyte solution. Unless removed from the electrolyte, the impurity concentrations increase until they interfere with the deposition of copper at the cathode.

The electrolyte is evaporated to increase the acid concentration and the impurities are electrolyzed using suitable electrodes. Arsenic and other impurities are deposited at the cathode, collected as a sludge at the bottom of the electrolytic cell in the vicinity of the cathode, and removed, U.S. Patent, 1956 (542); Kvyatkovskii et al., 1971 (541).

In purifying zinc electrolytes, iron, arsenic, and antimony are precipitated by autoclave precipitation. The temperature range is 90 to 200°C. Oxygen is required. Neutralizing agents such as CaO and NaOH are added. Arsenic precipitates as calcium or sodium arsenate, is filtered, and dried for commercial use, Savin, 1965 (493); Nelen, 1965 (549); and Scacciati, 1953 (570).

Solvent Extraction--

The preferential extraction of arsenic from an aqueous solution into an organic phase is a means of separating and concentrating arsenic. This technique of metal ion transfer from one liquid to another is called solvent extraction. It can be very effectively applied to arsenic extraction.

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The organic phase is normally considered to act as a solvent for the desired metal ions. The solvent is made selective toward a particular metal ion by the addition of a chelating agent, e.g., for arsenic, diethylammonium diethyldithiocarbonate (D.D.D.C), ammonium pyrrolidinedithiocarbamate (A.P.D.C.); methylisobutylketone (M.I.B.K.), etc.

Arsenic in the trivalent state can be extracted completely from sulfuric acid by DDDC, Wyatt, 1955 (601) or from hydrochloric acid solution, Veleker, 1962 (600). Toluene was used by Byrne, 1972 (590) to extract arsenic from sulfuric acid containing potassium iodide.

The extraction of arsenic from chloride solutions with tributyl phosphate and triethyl phosphate are reported by Auchapt, 1975 (699), and Daves, 1968 (512); from sulfuric acid solutions by Tserekova, 1970 (586).

Smithson et al., 1966 (598) have reviewed different techniques of liquid-liquid extraction of nonferrous metals including arsenic. Arsenic is separated from germanium in a mineral acid solution using dioctyldihydrogenmethylenephosphonate in lingroine. Other reagents are also mentioned. Press and Matveeva, 1969 (597) have discussed the results of their experimental study of arsenic extraction from certain pyrites and beneficiated ores. A chlorination roast followed by water leach was employed. Arsenic was effectively extracted with tryoctylamine in kerosene. Sovorovshaya and Minosyan, 1969 (599) have described the extraction of arsenic chloride by various solvents from complex solutions.

Many literature articles are available on arsenic recovery by solvent extraction. Our coverage of this area is not comprehensive because it falls outside the scope of the present project. The interested reader is referred to the large list of references quoted in the bibliography.

Ion Exchange--

Ion-exchange may not be of any commercial value for the production of arsenic because of the adequacy of other methods, however, ion-exchange may be successfully employed to remove arsenic from the electrolytes, waste waters, gas streams, pyrites, and beneficiated ores.

Separation is achieved by solid-liquid extraction or solid-solid extraction. The separation mechanism may be further sub-divided into categories according to the charge on the ion being exchanged, i.e., anionic exchange or cationic exchange.

Resins of anionic-exchange and cationic-exchange types have been employed in solid-liquid extraction of arsenic. Anion-exchange studies were made on germanium and arsenic in hydrochloric acid solution by Nelson and Kraus, 1955 (610). There was little adsorption of Ge (IV) and As (III) in dilute HCl solutions but the adsorption increased rapidly in stronger HCl solutions. The differences in adsorption characteristics as a function of acid concentration can be used to separate the various ions. Kholmanskikh

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et al., 1972 (606) also concluded that sorption rate of arsenic is higher on the anion-exchangers in the highly acidic solutions.

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Ion-exchange can be used to purify metal salt solutions. A USSR Patent 1972 (611) describes the process of removing arsenic from an acid solution containing CuSO_4 using an anionic exchanger. The solution containing the extracted arsenic was treated with H_2S gas and arsenic was precipitated as arsenic sulfide.

Kunin and Myers, 1947 (607) have studied the anion-exchange equilibria in an anion-exchange resin. The reactions of the acid adsorption, regeneration, and anion interchange types were included. They concluded that all three types of processes were true anion-exchange reactions in which the equilibrium for the various anions involved depended upon the structure and the valence of the anion as well as the ionization constant of the corresponding acid. The exchange "potentials" of the various anions were of the order: $\text{OH}^- > \text{SO}_4^{2-} > \text{CrO}_4^{2-} > \text{Citrate} > \text{tartrate} > \text{NO}_3^- > \text{AsO}_4^{3-} > \text{PO}_4^{3-} > \text{MoO}_4^{2-} > \text{Br}^- > \text{Cl}^- > \text{F}^-$.

Ion exchange has been used to separate arsenic from other metals in flue-dust leach liquor. Hartley, 1960 (605) cites one such example using a cation exchange resin to separate metal ions from arsenic. The arsenic containing solution can then be treated for arsenic recovery.

A U.S. Patent, 1958 (609) describes the use of mixed anionic and cationic exchange resins which deposit the metal, oxide, or complex. These deposits are eluted and a concentrated solution is obtained which is reacted with H_2 or CO in an autoclave at high temperature and pressure to precipitate the metal particles.

Activated kaolin can be used to adsorb arsenic from roaster gases, insecticides, and fungicides. Sieling, 1957 (210) has studied the role of kaolin in anion sorption and exchange mechanisms in soils. Zeolites activated with CuO may also be used to remove arsenic from the roaster gases, USSR Patent, 1936 (602).

Volatilization--

A fourth solution purification technique is volatilization from solution as a halogen or hydrogen compound; Sandell, 1959 (617); Kinsley, 1951 (614), Fernandez, 1971 (613); Madsen 1971 (615); Pollock, 1973 (616) and Braman, 1972 (612). The use of volatilization techniques described by the above authors can be considered to be useful for analytical separations or small scale batch operations. Commercial application is doubtful.

OTHER PROCESSES

The remaining literature on treatment processes to produce an arsenic containing solid is subdivided as follows: Adsorption, Waste Water Treatment, Arsenic Glasses, Cements, and Flotation Separation.

Adsorption

Adsorption is a process in which the molecular species of one substance becomes attached to the surface of the other, i.e., concentrated at the interface. Certain interfaces, such as the gas-solid one, have long been recognized as of great importance in catalysis. Adsorption at the solid-liquid interface has also been investigated, though the presence of a solvent complicates the mechanism by competing with the solute for positions at the interface, Rose, 1961 (632). Finally, the investigation of solid-solid interfaces is fundamental in the study of catalytic promoters and friction.

Veikhhertz and Shvartz, 1935 (636), and Kharmandaryan and Kopeliovich, 1936 (629) have discussed the results of their investigation on adsorption of arsenic by various silica gels. They concluded that the use of silica gel to adsorb arsenic in the form of As_2O_3 is uneconomical on the basis of the activity of silica gel.

Adsorption of As_2O_3 and As_2O_5 by metal hydroxides solutions has been investigated by the various authors. Of the Al, Cu, Sn, Fe, Cr, Zn, and Cd hydroxides studies by Jaroszewicz, 1958 (628), $Cd(OH)_2$ was found to be the most active adsorbent of As_2O_3 . This is in contrast to the study made by Boutaric and Perreau, 1928 (619) who found Zn and Mn hydroxides as the most active adsorbents. Although not the best adsorbent, $Fe(OH)_3$ was found to adsorb As_2O_3 in solution practically instantaneously. Lockemann and Lucius, 1913 (631) also investigated the total adsorption of As_2O_3 by ferric hydroxide. They found adsorption to be dependent on the temperature which does not concur with the observations made by Boutaric and Perreau who did not find any appreciable influence of temperature on the As_2O_3 adsorption by $Fe(OH)_3$.

A U.S. Patent, 1975 (621) describes the use of the coprecipitates of $Al(NO_3)_3$ and $Fe(NO_3)_2$ or $Co(NO_3)_3$ with NH_4OH . Essentially the coprecipitates are the metal hydroxides of Al and Fe or Co. The product is slurried, extruded into pellets, and calcined at 800 - 1500°F to achieve hardness and surface area. The pellets are used to adsorb arsenic from the synthetic crude oil flowing over them.

Ion-exchange resins have been employed to remove arsenic and other cations from the gases and the liquids, however, what is done as to the disposal or the recovery of the contaminants is not clear. Activated charcoal and zeolites are also used, Evadokimov and Kogan, 1969 (623), and Evadokimov, 1964 (622). Arsenic can be adsorbed onto the heated metal alloys, i.e., Cu-Zn, Cu-Sn, and Ga-Al alloys. Arsenic in the gas mixture forms thermally stable alloys with the former metal systems, Jap. Kokai, 1974 (633).

Soils and clays adsorb arsenic as As_2O_3 , arsenites, and arsenates depending on the conditions, e. g., availability of Fe_2O_3 , amount of calcium or other ions, and diminishing pH values. Calcium carbonate retains As_2O_3 as an arsenate under the right pH conditions, the arsenate remaining very stable in the pH range of 10-12, but the discharge of such effluent water poses a problem as the maximum pH allowed in the effluent water 8.5 to 9, Misra and

Tiwari, 1963 (199); Holobradý and Galba, 1969 (182); Shipnikiv, 1936 (634); and Hebert and Boischot, 1947 (180).

Waste Water Treatment

The removal of arsenic from the industrial waste waters as well as the drinking waters has been practiced for some time. Since in most areas, drinking water supplies contain arsenic much below the current health standard of 0.05 mg/liter, there has not been very many attempts to develop a technology for arsenic removal from the drinking water.

Shen, 1973 (659) describes the work he has done on arsenic removal from the groundwater of southwest Taiwan where arsenic is high in concentration. The water is treated with chlorine, coagulated with ferric chloride, and filtered. Bellack, 1971 (156) studied the arsenic removal problem from the waters of some regions in the southwest United States. He used activated alumina to remove the arsenic. Gullledge and O'Connor, 1973 (648); Nilsson, 1971 (250); Trelles and Bach, 1941 (661); Trelles and Amato, 1949 (660); a German (East) Patent, 1967 (649); Berezman, 1955 (641), all describe the techniques of removing arsenic from the drinking water using various reagents. Whitacre and Pearse, 1974 (65) have summarized the work done by some of the people mentioned above.

Industrial waste waters have been treated with various reagents to remove arsenic. Porubaev et al., 1972 (654) used different phosphates to remove arsenic. They claimed the highest degree of purification (99.91%) was obtained by using Ba, Fe, and Al phosphates and H_3PO_4 with controlled pH. Rosehart and Lee, 1972 (657); Furoshova, 1972 (646); Cladysheva et al., 1973 (647) and Cherkinskii and Ginzburg, 1941 (643); Skripach, 1970 (211); Nilsson, 1971 (250) have described their work on removing arsenic from the gold mine water, sewage water, and the other industrial waste water. They all used lime to precipitate arsenic. The discharge contained arsenic at much lower concentrations than the health standards required.

Power plant ashes have been utilized to adsorb arsenic through CaO available in the ashes. Dushina et al., 1974 (644); Rebrova et al., 1971 (655); and Okun, 1959 (652) claimed good results in arsenic removal.

Ross, 1973 (711) reviewed the removal of heavy metals from mine drainage waters by precipitation as oxides and hydroxides.

There are some other techniques available for treating the industrial waste waters; Revzin, 1958 (656); Jap. Kokai, 1974 (645); a USSR Patent, 1947 (658); and Milusheva et al., 1972 (651). None of the papers describes the eventual disposal of the precipitated arsenic, and in this regard the work on the removal of arsenic from the waters should be considered incomplete.

Arsenic Glasses

For purposes of this report the American Society for Testing Materials definition of glass will be used: Glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallizing.

Rawson, 1964 (677) states that the following pure oxides readily form glasses: SiO_2 , GeO_2 , B_2O_3 , P_2O_5 , and As_2O_3 . Each of the oxides in addition to being glass forming compounds may form glasses when combined with other non-glass oxides. But there are limits to how much additional oxide may be added and yet yield a glass forming system. Whether an oxide or combination of oxides form a glass depends on the rate of cooling. Some systems require very rapid cooling to retain the non-crystalline structure. Therefore, the quantity of liquid and the geometry of the cooling vessel may be such that a maximum cooling rate is attained that is not rapid enough to prevent crystallization. By decreasing the quantity of material or changing the geometry of the cooling system the cooling rate may be increased and a glass phase may possibly be retained. Some liquids may form a non-crystalline mass only if a very small quantity of liquid is cooled very rapidly. The product fits the description of a glass but the technique required to produce it negates its possible use for large scale operations.

Arsenic containing glasses may be classed as oxide glasses or sulfide glasses.

Arsenic oxide glass can be prepared by condensing oxide vapor on a cold surface. However, this type of glass is useless from the standpoint of storage in an environmentally safe manner because of its high solubility in water.

Binary glasses based on As_2O_3 in combination with other oxides have not been extensively studied. Their physical and chemical properties are unknown.

Formation of some arsenic oxide glasses was studied by Imaoka, 1962 (671). He reported the arsenic content of glasses for several binary compositions, Table 20. Heaton and Moore, 1957 (667) state that glasses were formed between As_2O_3 and PbO , K_2O , Sb_2O_3 , MoO_3 , SeO_2 and U_2O_5 .

There does not appear to be any reported studies on systems containing arsenic oxide plus two or more additional oxide compounds.

There are two reported studies on the disposal of arsenic containing wastes by its incorporation in a glass matrix. Lindblad, 1929 (673) has patented a process for treating arsenious acid by producing a slag (a slag is a glass-type by-product that is produced in many smelting operations). Lindblad produced a slag that he considered "remarkably constant and insensible to the influence of both water and carbonic acid and air, and can therefore be stored in the open air without any risk." Arsenic oxide was roasted in air with lime at 500°C to produce calcium arsenate. This compound was then smelted with a basic slag produced during the smelting of the original

ore. The melted product when cooled could then be disposed of along with the other slag reject material.

A similar process is described by Riemann, 1973 (678). "The arsenic containing waste is dried, granulated and added to a mineral melt which solidifies with closed pores, e., slag. Subsequently the cold material is water-treated to remove soluble waste from the open pores at the surface. The treated slag is deposited on garbage dumps."

Neither of the above two authors quote to what concentrations the arsenic can be incorporated in the slags or their test basis for claiming an environmentally safe product.

One study on the chemical stability of arsenic glasses was reported by Jochmann, 1964 (672). He treated low arsenic containing glasses in boiling water. His conclusion was that for glasses containing up to a few percent arsenic no arsenic extraction occurred. The history of arsenic use in glass is reviewed by Silverman, 1932 (680). Again this reference deals only with low arsenic glasses, i.e., less than 0.75 percent.

A second class of arsenic glass is the sulfur glasses.

A much wider range of glass-forming compositions between arsenic and sulfur than between arsenic and oxygen are possible, i.e., glasses can be formed in the sulfur-arsenic system between 10 - 65 percent arsenic but in the arsenic-oxygen system only As_2O_3 is a glass former; Flaschen, 1959 (664), 1960 (663).

Several ternary solutions have been studied, e.g., As - S - Se, As - S - Te, As - S - Tl, Flaschen, 1959 (664), 1960 (665); Hilton, 1963 (669), 1964 (670); As - S - Br, As - S - I, Flaschen, 1960 (663); Pearson, 1962 (675).

Very little data exist on the chemical stability of these glasses. In addition, the ternary glasses contain elements that are much too scarce and expensive for them to be considered disposable. Glaze, 1957 (666) reported that arsenic trisulfide has a low chemical stability. His conclusion concerning chemical stability was based on changes in surface properties in various solutions at various temperatures, times and acidity.

Cement

As_2O_3 has been used in Portland cement manufacture for special properties, e.g., retarded early-settling-time, early-high-strength, and resistance to chemical action of water. Also, As_2O_3 when mixed with concrete to encase timber piles intended for use in the construction of fishing harbours prevents attack of marine borers on the timber piles, Anon., 1935 (681) and Palen, 1935 (686).

Arsenates and arsenious oxide when mixed with Portland cement act as retarders against too rapid hardening of cement slurries, Lieber, 1973 (685) and a U.S. Patent, 1932 (689). According to Czamarska, 1966 (682) and Grzymek, 1959 (683), arsenic influences the formation of tricalcium silicate resulting from the reaction between $\text{Ca}_2(\text{SiO}_4)$ and CaO and reduces the speed of Ca_3SiO_5 formation.

Mixture of Portland cement and white arsenic works as a water-resistant cement, Werner, 1930 (690). A mixture of 30 percent arsenious oxide which is produced in large quantity as a by-product in smelting operations, and 70 percent Portland cement, after heating to about 250°C , forms a material with a normal set and markedly greater resistance to the chemical action of water.

The Boliden Mining Company resorted to mixing the cement with the arsenic trioxide which is produced in a large amount in processing its arsenical gold ores. The mixture was made into blocks, dried, and dumped out at sea. The practice of As_2O_3 disposal turned out to be rather expensive, and an alternate disposal method was sought, Davis et al., 1971 (700).

Flotation Separation

There is available a tremendous amount of information on flotation of arsenopyrite ores. Since the accumulation of the information on arsenopyrite ore flotation was considered beyond the scope of this literature survey, the flotation data of such ores are being left out. On the other hand, there is not much information on the flotation of the flue dust in order to concentrate arsenic.

In one case, U.S. Patent, 1941 (692), flue dust was subjected to a froth flotation operation. The metallurgical flue dust is mixed with a little water and coal oil and floated. The concentrate is substantially in the pure form of As_2O_3 . The filtrate along with the spent liquor from the flotation cell is recycled to mix with more flue dust.

A selective flotation is applied to the ores to prevent arsenic from going into the concentrates. Bulandr, 1965 (693) has applied this technique of selective flotation to the copper ores from Slovinski region in Czechoslovakia. Waste tailings from gold milling operations have been re-worked to extract precious metals in association with arsenic by flotation, Tabukopulo and Tarasov, 1957 (698) and Dobrescu, 1958 (694).

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